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CHEMISTRY DIVISION

QUARTERLY PROGRESS REPORT

FOR PERIOD ENDING SEPTEMBER 30, 1951

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S. C. Lind, Acting Director
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QUARTERLY PROGRESS REPORT

for Period Ending September 30, 1951

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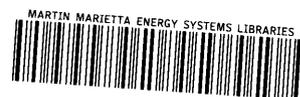
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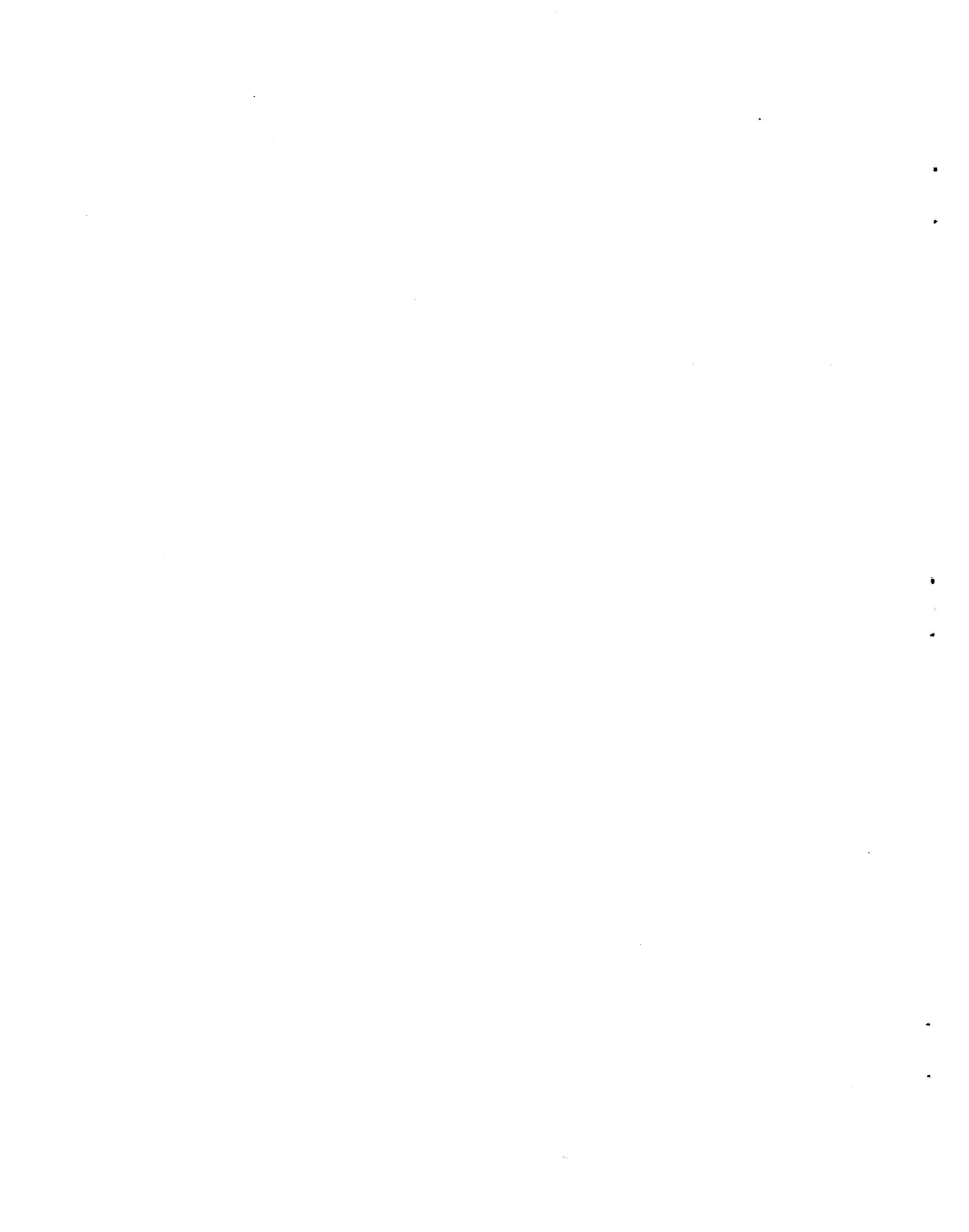
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ABSTRACT

INORGANIC CHEMISTRY

Solid thorium perchlorate prepared by fuming thorium nitrate hydrate to dryness with perchloric acid is found to be partially hydrolyzed. The formula $\text{Th}(\text{OH})_2(\text{ClO}_4)_2$ or $\text{ThO}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ approximates the composition determined by several methods of analysis.

By ultracentrifugation the polymerization of zirconium [0.05 M Zr(IV) in 0.1 M HCl-1.9 M NaCl solution] appears to be less (mol wt about 1000) than in perchlorate medium of equal acidity. Zirconium (0.12 M in 1 M HClO_4 -1 M NaClO_4) is still monodisperse at a higher concentration and carries a substantial charge. The unknown size of this charge makes a definite assignment of molecular weight doubtful.

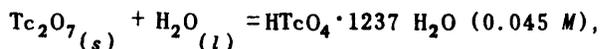
The solubility of zirconium(IV) in concentrated hydrochloric acid and lithium chloride solutions, and the solid phases separating in these solutions are being studied.

The freezing-point depressions of uranyl fluoride solutions are being investigated using a Thermistor that is accurate to 0.01°C for measuring temperature.

Using tracer techniques, the adsorption of zinc from hydrochloric acid solutions (0.1 to 2 M) by Dowex-1 indicates the anion to be ZnCl_4^{2-} . A maximum of adsorbability occurs near 3 M HCl.

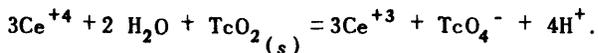
The cation adsorption of zinc at equilibrium with Dowex-50 at room temperature has been studied in HCl and HClO_4 solutions (0.1 to 5 M). The adsorbability in chloride solution is approximately the same as in perchlorate solutions at low ionic strength ($\mu=0.05$) but is less than in perchlorate at high ionic strength. The investigation is being extended to higher temperatures.

Study of the chemistry of technetium has yielded the following results:



$$\Delta H = -11.6 \text{ kcal/mole.}$$

The heat of formation of Tc_2O_7 is being investigated. TcO_2 has been prepared by heating NH_4TcO_4 , and the formula of Fried was verified by dissolving TcO_2 in excess ceric solution and back titrating with iodide solution,



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Attempts to prepare TcO_3 have not succeeded, but further efforts are planned. Redox potentials are being studied. The magnetic susceptibilities of NH_4TcO_4 , Tc_2O_7 , TcO_2 , and Tc will be measured.

New experiments are planned in the study of exchange $Br_2-BrO_3^-$ using bromine-82 as tracer.

NUCLEAR CHEMISTRY

The decay scheme and gamma ray energies of gallium-67 prepared by proton bombardment of zinc in the ORNL 86-in. cyclotron have been studied. The present result, which is of sufficient accuracy for therapeutic use, will be checked by other methods.

The absolute and relative fission yields of xenon and krypton have been redetermined by dissolving Hanford slugs in hydrochloric acid solution: xenon-135, 6.1%; the two isomers of krypton, 1.51%. Corrected fission-yield curves are shown.

Final purification of technetium from Chalk River metal wastes is being effected by distillation of tetraphenyl arsonium pertechnetate and tetraphenyl arsonium perchlorate from sulfuric acid solution refluxed in a quartz still at $300^\circ C$ to destruction of all organic matter. Intensity of color of successive samples, roughly proportional to the concentration of technetium, is to be attributed to hydration rather than to oxidation states.

RADIO-ORGANIC CHEMISTRY

Radiation, Analytical, and Preparative Chemistry

Radiation chemistry. The effects of gamma radiation from a cobalt-60 source upon labeled acetic acid in

aqueous solution have been studied. Preliminary identifications of the products of the action of the radiation have been made by paper chromatography. The gamma-radiation induced synthesis of succinic-2,3- C^{14} acid from acetic-2- C^{14} acid has been investigated.

Analytical chemistry. Synthetic mixtures of formic- C^{14} , acetic-1- C^{14} butyric-1- C^{14} , and valeric-1- C^{14} acids were separated chromatographically as their diethylamine salts. This work was carried out as an aid to the identification of these compounds in solutions which have been irradiated with a cobalt-60 source.

Preparative chemistry. Butyric-1- C^{14} acid, 21.1 mc, and valeric-1- C^{14} acid, 8.64 mc, were prepared by conventional Grignard syntheses. Some procedures leading to the synthesis of valeric-2- C^{14} acid and trimethyl- C^{14} -acetic acid were developed. These compounds will be used in radiation chemistry studies.

Isotope Effect Studies. The carbon-14 isotope effect was studied for several reactions, with the following results: A normal isotope effect is indicated when the sodio derivatives of 1- and 1,2-substituted fluorenes are carbonated with carbon-14 dioxide, and in the thermal decomposition of mercurous formate- C^{14} . No isotope effect is indicated in a reaction of *p*-nitrophenyldiazonium chloride with butadiene-1- C^{14} , in the Diels-Alder reaction of 2,3-dimethylbutadiene with β -nitrostyrene- α - C^{14} , and in the addition of water to diphenyl (acetylene-1- C^{14}).

In addition, the carbon-13 isotope effect in the dehydration of formic- C^{13} acid has been measured to be about one-half the carbon-14 effect in formic- C^{14} acid at the same temperature.

Studies on the Mechanisms of Organic Reactions

Isotope-exchange reactions involving the carbon-carbon bond. Isotope-exchange studies with carbon-14 labeled reactants have shown that the Friedel-Crafts acylation reaction is irreversible. Neither extreme activation nor deactivation of the aromatic system by the introduction of groups has been found to facilitate exchange.

A number of base-catalyzed aldol-type condensations have been found to be reversible by this exchange technique.

Effect of aluminum chloride on ethylbenzene. The ethyl group, labeled with carbon-14 in the beta position to the ring, undergoes no isomerization when ethylbenzene is converted by aluminum chloride to diethylbenzene. Ethyl- β -C¹⁴ chloride, which underwent no isomerization when condensed with benzene, was isomerized quickly in the absence of the aromatic compound.

Test for the reversibility of the sulfuric acid dehydration of formic acid. An attempted exchange reaction between carbon-14 monoxide and formic acid in sulfuric acid solution has demonstrated that the reversibility of the formic acid dehydration reaction is negligible.

Displacement of the benzoyl group from phenyl 9-fluorenyl ketone. The existence of an equilibrium between 9-benzoyl-9-fluorenylcarbinol, phenyl 9-fluorenyl ketone, and formaldehyde has been demonstrated by chemical methods and by carbon-14 exchange studies.

Rearrangements of α -Diketones. Methyl phenyl diketone has been shown to rearrange to atrolactic acid in

alkaline solution by 100% migration of the phenyl group. These results, which are identical with those obtained in the rearrangement of α,α -dibromopropiophenone, indicate the possibility that the diketone is the intermediate in the conversion of the dibromide to atrolactic acid.

Structure Determination Studies. Model experiments have been completed for the structure proof of 1-methylphenanthrene-9(10)-C₁¹⁴ and chrysene-5,6-C₁¹⁴.

CHEMISTRY OF SEPARATIONS PROCESSES

Study of the removal of protactinium from ThF₄ by volatilization at high temperatures has been continued. Covolatilization with PtF₄ at 600°C enhances the removal and suggests investigation of the influence of other volatile fluorides.

The desire to process D₂O solutions used in the homogeneous reactor by ion exchange in resins or organic solvents in which only the readily replaceable hydrogen atoms are deuterated raised a question as to the extent of undesired exchange between D₂O and ordinary hydrogen in the organic phase under radiation. Experiments have been started to determine the exchange by measuring the water density.

The products of the hydrolysis of tri-*n*-butyl phosphate are being prepared in pure form, both with and without labeled phosphorus. These are to be used for carriers and tracers in analysis of the products.

Dibenzoylmethane is found to be much less effective than TTA (thenoyltrifluoroacetone) in extracting Zr⁺⁴ or UO₂⁺² from aqueous solution.

The chromatographic separation of thenoyltrifluoroacetone from its

CHEMISTRY DIVISION QUARTERLY PROGRESS REPORT

metal chelates in different solvents by a series of solid adsorbents was investigated (Table 10).

Self-diffusion of several types of ions has been studied in Dowex-50 type sulfonic acid cation exchangers, in Dowex-1 type anion exchangers, and in a chelating resin exhibiting high specificity for transition group elements.

CHEMICAL PHYSICS

The crystal structure of KDF_2 and of KHF_2 has been investigated by neutron diffraction. The use of single crystals is advantageous and eliminates the need of deuterated compounds. The results support the single potential minimum in agreement with the thermodynamic study of Westrum and Pitzer. Work is in progress on the structure of ammonium chloride, vitreous silica, palladium and platinum oxides, and potassium dihydrogen phosphate.

Preliminary experiments toward the use of molecular beams in chemical kinetics are being continued.

Radio frequency spectroscopy is being used to study quadrupole coupling at low temperatures. Frequencies are reported (Table 15) at 77, 20, and 4°K for ten chlorine and fluorine substitution products of methane and for Cl_2 . Quadrupole transitions were also determined for ClF and ClF_3 , $AsCl_3$, $SiCl_4$. The ratio of quadrupole moments of chlorine-35 and chlorine-37 (1.26878) is now in good agreement with that of others.

A new type of spectral lines insensitive to a magnetic field have been discovered but not yet interpreted. They are numerous, broadly distributed over a wide spectral arc, and quite variable in intensity.

They have been observed in several of the compounds under investigation.

In the calorimetric measurement of the heat evolved in the radioactive decay of carbon-14, contained as $C^{14}O_2$ in a mixture with $C^{12}O_2$, the percentage of $C^{14}O_2$ in the mixture was determined with a gas-density balance. The apparatus and technique of the measurement are described. Final evaluation of the results has not yet been made.

RADIATION CHEMISTRY

The various aqueous uranyl solutions which might be used in a homogeneous reactor are being irradiated to determine the chemical reactions induced, especially the liberation of gas. By sweeping a solution during gamma radiation with helium gas, SO_2 was removed and measured from 18 and 11 M H_2SO_4 ; none was detected from 0.4 M H_2SO_4 or 1.25 M UO_2SO_4 solution.

Irradiation in the Oak Ridge pile of natural uranium sulfate and fluoride in concentrations of 44.6 and 297 g U/liter were made at temperatures of 30, 100, and 150°C (Table 17). The yield of hydrogen (about 1 molecule/100 ev) is considerably lower than under alpha radiation of aqueous solutions. The initial excess of hydrogen over oxygen (due to the formation of H_2O_2) is highest under conditions of greater stability of H_2O_2 , namely lower temperature and radiation intensity. Energy absorption was determined calorimetrically. Silica containers were used.

The study of the effect of gamma radiation on the catalyst ZnO in inducing the reaction between H_2 and C_2H_4 has been continued. Positive results have been obtained showing diminution of the catalytic activity, though definite proof of the nature of the effect of X-rays on the ZnO has not yet been obtained.

CHEMISTRY OF THE SOLID STATE

The high-temperature X-ray diffraction spectrometer has been operated at 2100°C.

The construction of the remote-control X-ray diffraction spectrometer is nearly complete.

The irradiation of yellow and red plumbous oxide with ultraviolet, X, and gamma rays was found not to lead to a phase transformation from yellow to red as had been reported in the literature but to the production of color centers easily removable by slight heat, and, in the case of ultraviolet light, to some chemical decomposition.

The irradiation of sodium bitartrate and arsenous oxide in the cobalt gamma-ray source did not destroy the crystal structure, and is thus distinct from effects, previously reported, of reactor and alpha-particle irradiation.

The experimental investigation of fused salt-excess metal systems has been started.

INSTRUMENTATION

The efficiency of the scintillation counter for gamma-ray counting has been tested in detail (Figs. 18, 19, and 20). A crystal of sodium iodide activated with thallium best meets the requirements of high density, large light output per unit of gamma energy lost in the crystal, and good optical properties. It is recommended that measurements of radioactivity of liquid or solid samples should be made by gamma counting whenever possible.

A new method and an alternate simplified method are described to

determine the dead time of an amplifier or scaler. The advantages of these methods are compared with those of the two methods previously used (Figs. 21 and 22).

Two power suppliers for scintillation counting are described. The high-voltage output of one is positive and of the other negative, with respect to the ground. A unit to supply both polarities is not feasible. Circuit diagrams are shown in Figs. 23 and 24.

REACTOR CHEMISTRY

Data for the solubility of UO_3 in H_3PO_4 solutions at 250°C are shown in Table 21. The composition of solution and solid phase are also given for room temperature, 200, and 260°C.

Determination of the solubility of lanthanum and yttrium sulfates has been extended to 1.26 M UO_2SO_4 . Investigations are also in progress on the solubility of cesium, cerium, and zirconium sulfates in 1.26 M UO_2SO_4 . Additional studies of the solubility of fission product sulfates in uranyl sulfate solutions includes $SrSO_4$, Ag_2SO_4 , $Zr(SO_4)_2$ and $Ru_2(SO_4)_3$.

The conductivity of UO_2SO_4 solutions from 0.05 to 1.25 M has been determined at 25°C.

The vapor pressure of 0.126 and 1.26 M UO_2SO_4 has been measured from 200 to 350°C. Data and details will be reported in the Homogeneous Reactor Project quarterly report for the period ending November 15, 1951.

Experiments on stability of UO_2SO_4 solutions under different conditions of temperature, concentration, radiation, and gas volume and pressure disclosed that the uranyl ion catalyzes the recombination of hydrogen and

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oxygen in solution. A search for other polyvalent ions having the same property revealed that the cupric ion at low concentration (up to 400 ppm) exerts a much greater catalytic effect than uranyl ion (135,000 times that of UO_2^{++}). Other ions are now under investigation.

A survey of the stability of fuel solutions in contact with metallic titanium, zirconium, and pretreated stainless steel has been made in quartz ampoules at 250°C.

Uranium-235 enrichment of UO_2SO_4 solutions raises the equilibrium pressure of hydrogen and oxygen owing to the greater proportion of fission energy.

In pursuance of electrochemical corrosion studies an attempt is being

made to develop a high-temperature reference electrode. Three systems are being tried: Pb/PbSO_4 ; $\text{Ag/Ag}_2\text{SO}_4$; and $\text{Pt/PbO}_2 + \text{PbSO}_4$.

The mechanism of the corrosion process of stainless steel in contact with uranyl sulfate solution at 250°C is being investigated electrochemically. The corrosion products, the solution changes, and the gases evolved have been measured. The anodic and cathodic reactions have been studied. The presence of oxygen tends to suppress corrosion and promote self-healing of the protective film. Rapid movement of the solution stifles self-healing by removing the metal ions before they can reprecipitate in place. Gas analysis is the best means of following the corrosion process.

CHEMISTRY DIVISION QUARTERLY PROGRESS REPORT FOR PERIOD ENDING SEPTEMBER 30, 1951

INORGANIC CHEMISTRY

CHARACTERIZATION OF SOLID THORIUM PERCHLORATE

W. C. Waggener R. W. Stoughton

Solid thorium perchlorate prepared by fuming thorium nitrate hydrate to dryness with perchloric acid at 200 to 215°C has been found to be partially hydrolyzed. Its composition is approximately $\text{Th}(\text{OH})_2(\text{ClO}_4)_2$ or $\text{ThO}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, as determined from the analyses: (1) thorium, by precipitation and ignition of the oxalate to the dioxide, and (2) hydroxyl (or hydroxyl equivalent), by titration with acid. In addition, perchlorate has been determined by two methods. The first method consisted of precipitating and weighing as the tetraphenylarsonium salt. The second involved absorption of the thorium on a cation-exchange resin and titration of the eluted hydrogen ion. These analyses indicated a similar formula. However, the results obtained thus far in these latter measurements are not sufficiently concordant for reporting in detail.

It is planned to continue the study of the aqueous thorium-thenoyltrifluoroacetone (TTA) system, as previously outlined,⁽¹⁾ upon completion of this investigation of the solid thorium perchlorate.

⁽¹⁾W. C. Waggener and R. W. Stoughton, "Aqueous-Benzene-TTA Extraction Method," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1951*, ORNL-1053, p. 18.

ULTRACENTRIFUGAL EXPERIMENTS

J. S. Johnson K. A. Kraus

ZIRCONIUM SOLUTIONS

An equilibrium ultracentrifugal run on about 0.05 M Zr(IV) in 0.1 M HCl-1.9 M NaCl solution indicated that the zirconium was present in a mixture of species with an average molecular weight of about 1000. The zirconium thus appears to be less polymerized in chloride than in perchlorate media of this acidity.⁽²⁾

A run of about 0.12 M Zr in 1 M HClO₄-1 M NaClO₄ indicated that the zirconium is still essentially monodisperse at this higher concentration, and that as before in chloride-free solutions the polymers carry a substantial charge. The unknown size of this charge makes a definite assignment of molecular weight to the polymers doubtful. There seems little question, however, that continuous polymerization of the type postulated by Connick and Reas for similar conditions does not occur.⁽³⁾

THORIUM SOLUTIONS

Studies of the degree of polymerization of thorium(IV) hydrolysis products are under way.

⁽²⁾J. S. Johnson and K. A. Kraus, "Ultracentrifuge Studies of Inorganic Systems," *loc. cit.*, p. 18.

⁽³⁾R. F. Connick and W. H. Reas, "The Hydrolysis and Polymerization of Zirconium in Perchloric Acid Solutions," *J. Am. Chem. Soc.*, 73, 1171 (1951).

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SOLUBILITY OF ZIRCONIUM(IV) IN CHLORIDE SOLUTIONS

J. S. Johnson K. A. Kraus

Preliminary experiments have been carried out on the solubility of zirconium(IV) in concentrated hydrochloric acid and lithium chloride solutions. It is hoped that the measurements will yield eventually some information regarding the species existing in the solutions. It was found that in moderately concentrated solutions the solubility of zirconium(IV) is considerably lower in lithium chloride than in hydrochloric acid. For both media the solubility appears to go through a minimum near 9 M chloride.

The solid phases separating from both hydrochloric acid and lithium chloride solutions have been submitted to the X-ray group for identification. According to Ellison and Bredig, the phases separating from both solutions appear to be the same. However, there is some question as to whether the phase separating from the solution is identical with that obtained on partial drying of the samples.

Purification of the necessary reagents is now in progress for a more complete determination of the solubilities.

MEASUREMENT OF FREEZING-POINT DEPRESSIONS OF URANYL FLUORIDE

J. S. Johnson K. A. Kraus

Equipment is being assembled to measure freezing-point depressions of uranyl fluoride solutions. Earlier data by Secoy⁽⁴⁾ indicated that the

⁽⁴⁾C. H. Secoy, "The Mean Activity Coefficients of Uranyl Fluoride in Water Solutions at 25°," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, ORNL-795, p. 28.

freezing-point depressions of uranyl fluoride were abnormally low. The precision of the data at high uranyl fluoride concentrations, however, was not sufficient to permit an unequivocal interpretation in terms of association constants and activity coefficients of undissociated uranyl fluoride.⁽⁵⁾

It is planned to measure temperatures with a Thermistor which has a temperature coefficient of resistance of approximately 5%/°C⁽⁶⁾. The Thermistor, which has a resistance of approximately 0.5 megohm, is put in series with a 1-megohm resistor, and the voltage drop across the Thermistor is measured with a vibrating reed. It appears possible to reproduce freezing-point depression to about 0.01°C. Calibration of the Thermistor with respect to a platinum-resistance thermometer is now in progress.

ANION EXCHANGE OF ZINC IN CHLORIDE SOLUTIONS

F. Nelson K. A. Kraus

Work on the anion-exchange behavior of zinc in hydrochloric acid solutions (0.1 to 12 M) has been extended, and distribution coefficients have been measured with Dowex-1 using tracer techniques. The results are shown in Fig. 1. As with most of the transition elements, adsorbability of zinc from concentrated hydrochloric acid solution is considerably lower than with iron(III) or gallium(III), suggesting that the adsorbed species has a higher charge than minus one (probably $ZnCl_4^{=}$). The adsorbability

⁽⁵⁾K. A. Kraus and J. S. Johnson, "Undissociated Species and Dimerization in Aqueous Solutions of Uranyl Fluoride," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951*, ORNL-1116.

⁽⁶⁾J. A. Becker, C. B. Green, and G. L. Pearson, "Properties and uses of Thermistors," *Bell System Tech. J.*, 26, 170 (1947).

goes through a maximum near 3 M HCl, where $ZnCl_4^{2-}$ is probably the principal species in solution. A more detailed analysis of the data is being made.

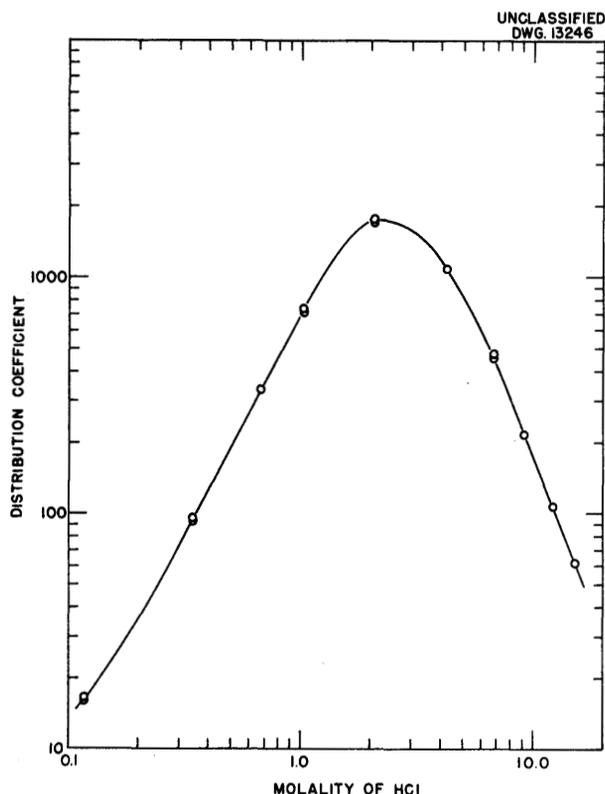


Fig. 1. Absorption of Zinc (II) by Dowex-1 from HCl Solutions.

CATION EXCHANGE OF ZINC IN CHLORIDE AND PERCHLORATE SOLUTIONS

R. A. Plane, K. A. Kraus

The adsorbability of zinc by the cation-exchanger Dowex-50 has been studied in hydrochloric acid and perchloric acid solutions in the range 0.1 to 5 M using equilibrations at room temperature.

It was found that the adsorbability in perchlorate solution varies with ionic strength approximately as

predicted from the mass action expression

$$K_{ar}^m = \frac{(Zn^{++})_r (H_3O^+)^2}{(Zn^{++}) (H_3O^+)_r^2}$$

where K_{ar}^m is the mass action constant, the parentheses indicate concentrations, and the subscript r indicates the resin phase. The deviations of K_{ar}^m from constancy (Fig. 2) are probably due to the changes in the proper activity coefficient ratio.

As also shown in Fig. 1, the adsorbability in chloride solutions is approximately the same as in perchlorate solutions at low ionic strength ($\mu = 0.05$), and it is less than that in perchlorate solutions at high ionic strength. This decreased adsorbability is probably due to chloride complexing of zinc(II). A more detailed interpretation is in progress.

Experiments are now under way to study the relative adsorbability in perchlorate and chloride solutions at elevated temperatures, in an attempt to evaluate the temperature coefficients of the equilibria.

CHEMISTRY OF TECHNETIUM

J. W. Cobble, G. E. Boyd
W. T. Smith, Jr.*

CALORIMETRY OF TECHNETIUM COMPOUNDS

Heat of Solution of Tc_2O_7 . The heat of solution of technetium heptoxide in water to form dilute solutions of pertechnic acid is being studied as part of the program of collection of thermodynamic data on technetium

*Professor of Chemistry, University of Tennessee, and ORNL Consultant.

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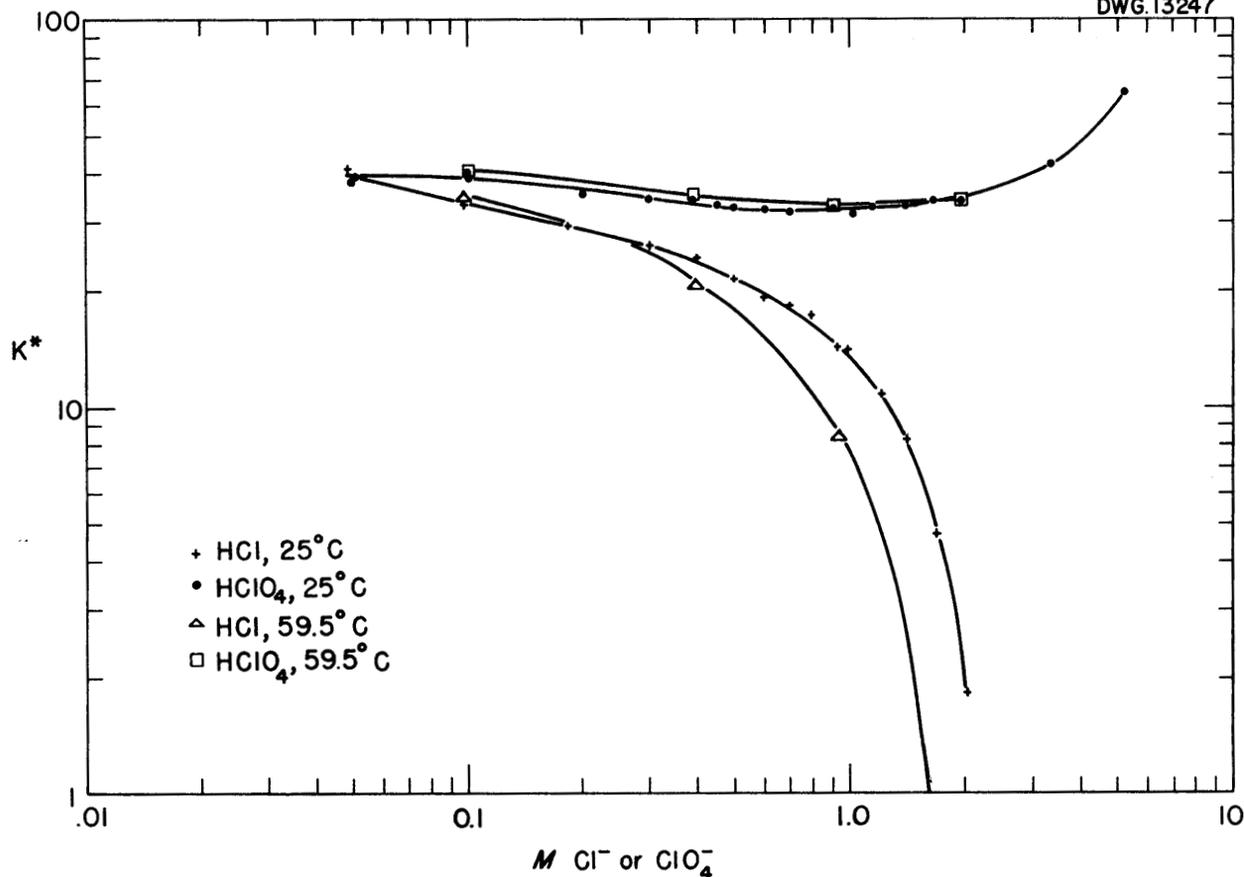
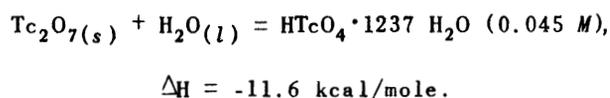


Fig. 2. Cation Exchange of Zinc in Chloride and Perchlorate Solutions at 25°C and 59.5°C (Tracer Loading).

compounds. A microcalorimeter was constructed from a 50-ml Dewar flask which was fitted with a ground-glass stopper into which two pieces of glass tubing were sealed to provide inlets for a motor-driven stirrer and a quartz-enclosed, calibrated, platinum-resistance thermometer. The whole assembly was submerged 6 in. below the level of a large thermostat (controlled to $\pm 0.002^\circ\text{C}$) to minimize thermal leakage. The apparatus has a thermal-leak modulus of $2.4 \times 10^{-3} \text{ min}^{-1}$, or about 0.1 cal/min-deg, so that temperature changes of ~ 0.2 deg may be measured to $\pm 1\%$. This corresponds to a heat measurement of about 10 to 20 cal to the same ac-

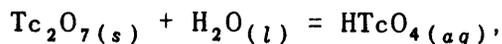
curacy. The calorimeter was calibrated by the heat evolved upon breaking a weighed amount (about 1 ml) of 1 N HCl contained in a thin bulb into about 30-ml of a solution of NaOH (1 milliequivalent, slight excess over the HCl).

Preliminary experiments have given a value of -11.6 ± 1 kcal/mole for the following reaction:



By analogy to perrhenic acid, the

heat of dilution of which is negligible at this concentration,⁽⁷⁾ it is possible to write



$$\Delta H = -11.6 \pm 0.1 \text{ kcal/mole.}$$

The technetium heptoxide samples dissolved were about 200 mg.

Heat of Formation of Tc_2O_7 . Preparations to measure the heat of formation of Tc_2O_7 from its elements are being made. A procedure based on the work of Roth and Becker⁽⁸⁾ on rhenium will involve the combustion of technetium metal in paraffin oil with 30 atm of oxygen. Paraffin oil is necessary since the element burns rather slowly unless a high ignition temperature is provided. The heat of formation of the TcO_4^- ion may be calculated from the heat of formation and solution of the heptoxide. An estimate of the free energy of formation may be made using a reasonable entropy of formation.

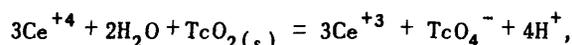
PREPARATION OF TECHNETIUM OXIDES

TcO_2 . Fried⁽⁹⁾ has reported the preparation of a black lower oxide of technetium formed by heating NH_4TcO_4 , which was assumed to be TcO_2 . This assumption has been verified quantitatively. About 20 mg of NH_4TcO_4 was heated for about 1 hr in a sealed quartz tube at slowly increasing temperatures up to 300°C. The ammonium salt first began to volatilize and then was rapidly decomposed into a jet black material. On cooling, drops of water were formed suggesting

that the following reaction proposed by Fried is substantially correct:



The black product can be dissolved by heating it in an excess of ceric sulfate solution. When 3.18 mg of the product was dissolved in an excess of standard ceric solution and back titrated with standard iodide an equivalent weight of 44.0₂ was found. If the oxidation reaction were logically assumed to be



the molecular weight would be 132 ± 1; the formula weight for TcO_2 is 131.

A jet black material of similar appearance was also formed when acidic solutions of pertechnetate were reduced by a magnesium ribbon. The formula for this compound, presumably also TcO_2 , has yet to be determined.

The direct potentiometric titration of $\text{TcO}_2(s)$ with ceric ion is a very slow process and does not appear to be suitable for its direct analysis. It has, however, provided an estimation of the potential for the $\text{TcO}_2-\text{TcO}_4^-$ couple of -0.6 v.

TcO_3 . Attempts to prepare TcO_3 by reduction of Tc_2O_7 with dry dioxane in a manner analogous to that reported for rhenium⁽¹⁰⁾ have not been successful. On one occasion Tc_2O_7 was reobtained. On another occasion a red material was formed that dissolved in water to give a transient red solution, reminiscent of HTcO_4 , which almost immediately decomposed to give a black precipitate (TcO_2 ?). By analogy to rhenium, TcO_3 might be

(7)W. A. Roth and G. Becker, "Physical Chemistry of Rhenium," *Z. physik. Chem.*, A159, 27-39 (1932); "Heats of Formation of Rhenium Oxides," *ibid.*, 415-16.

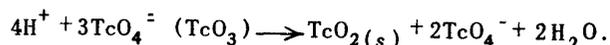
(8)*Ibid.*

(9)S. Fried et al., private communication.

(10)A. D. Melaven et al., *Inorganic Synthesis* (New York: McGraw-Hill Book Co., 1950), 3, 186.

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expected to disproportionate in acidic aqueous solutions:



Attempts to prepare TcO_3 by gaseous reduction of $\text{Tc}_2\text{O}_7(s)$ directly with carbon monoxide are planned.

REDOX POTENTIALS

Cells of the type

Pt/TcO ₂ ; HTcO ₄	KCl KNO ₃	HCl; H ₂ (g)/Pt,
---	-------------------------	-----------------------------

and

Pt/TcO ₂ ;	KTcO ₄ KOH	KCl KNO ₃	KOH; H ₂ (g)/Pt,
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are being set up to measure the potentials for the redox reaction:



An identification of the solid TcO_2 preparations by means of their X-ray diffraction patterns will be made in order to avoid the sort of trouble experienced with various crystalline modifications and imperfect compounds that have complicated measurements of the MnO_2 - MnO_4^- couple.

MAGNETIC STUDIES OF TECHNETIUM COMPOUNDS

C. M. Nelson G. E. Boyd
W. T. Smith, Jr.

The apparatus for measuring magnetic susceptibilities has been assembled and tested. Calibration experiments are in progress using small samples of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, and Pt. Owing to various breakdowns and leaks, these experiments have not been completed. However, they should be finished shortly and the technetium experiments started. The first samples to be measured will

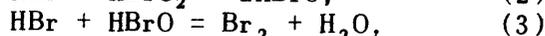
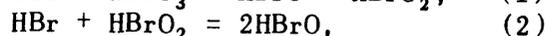
be of NH_4TcO_4 , Tc_2O_7 , TcO_2 , and Tc. Other valence states of technetium will be studied as soon as methods for their preparation can be worked out.

Br₂-BrO₃⁻ EXCHANGE USING BROMINE-82 AS TRACER

O. E. Myers

Discussion with R. H. Betts of the Chalk River Project has revealed that his experimental work⁽¹¹⁾ on Br_2 - BrO_3^- exchange and the work at this laboratory are in good agreement. Betts has not been able to correlate isotopic-exchange data with kinetic and thermodynamic data on the several oxidation states of bromine, but further discussion with Betts, H. Taube, and J. W. Kennedy, and a detailed mathematical analysis have resulted in a new approach to the problem. It now appears that the correlation may be made with some additional experimental work.

The exchange is considered to involve the following reactions:



The kinetic data can be accounted for reasonably well if one assumes that both reactions 1 and 2 are slow and that they are of the same order of magnitude. Present evidence all but excludes the possibility that reaction 2 is appreciably faster than reaction 1 under the conditions used in this work. Reaction 3 is assumed to be always at equilibrium.

If reaction 2 is slow, then there should exist an appreciable concentration of HBrO_2 during the course of the reaction; if it can be detected, this picture of the entire kinetic system can be verified.

(11) R. H. Betts and A. N. MacKenzie, "Isotopic Reactions in the System Bromine-Bromate-Hypobromous Acid," *Can. J. Chem.*, 29, 655-66 (1951).

NUCLEAR CHEMISTRY

DECAY SCHEME OF GALLIUM-67

A. R. Brosi B. H. Kettelle
 H. Zeldes

The Medical Division of the Oak Ridge Institute for Nuclear Studies has been interested for some time in the possible use of gallium radioisotopes in radiotherapy. Their interest recently has been in gallium-67, which has been produced in high specific activity by proton bombardment of zinc in the ORNL 86-in. cyclotron. Although this isotope was discovered in 1938 and has been studied by several workers,⁽¹⁾ the data are not complete enough to permit calculation of radiation dosages. A more complete study of gallium-67 is reported below.

The scintillation-spectrometer gamma spectrum shows the definite presence of a previously unreported 390-keV gamma ray, as well as the probably presence of an 800-keV gamma ray in low intensity. The spectrometer data also show that the 180-keV gamma ray has a higher intensity than the sum of the 390- and 297 keV transitions. The thin-lens spectrometer data show that only the 94-keV gamma ray is internally converted to an appreciable extent. Therefore, the 180-keV transition cannot terminate at the 390-keV level in zinc-67 as previously proposed.

In order to check this conclusion coincidences were measured between the conversion electrons of the 94- and 180-keV gamma rays. Since no true coincidences were found, the above conclusion that the 180-keV transition does not terminate at the 390-keV level was supported. Since

the sum of the energies of the 94- and 297-keV transitions is the same as that of the 390-keV transition, this latter gamma ray probably results from a crossover transition, and coincidences between the 94- and 297-keV gamma rays should be expected. Coincidence measurements between the conversion electrons of the 94- and 297-keV gamma rays showed that true coincidences occurred. However, the number of such coincidences was lower by an order of magnitude than would be expected from the counting yields of the two radiations.

Further work showed that true coincidences also occurred when the 297-keV gamma-ray pulses were delayed. A series of measurements with different delay lines showed that the 94-keV transition was from a metastable level that decayed with an 8.5- μ sec half-life. In addition to the delayed 297-keV-gamma conversion-electron coincidences, prompt 180-keV gamma-X-ray coincidences were measured. These data, along with a calibration of the conversion-electron counting yield on the thin-lens spectrometer, make it possible to compute the conversion coefficient of the 94-keV gamma ray, the disintegration rate of the sample, and the fraction of the disintegrations that go through the 94-keV level.

From the intensities of the 180-, 297-, and 390-keV gamma rays, as determined with a calibrated scintillation spectrometer, the number of capture processes to the ground state can be computed by difference. A decay scheme showing the energy levels in zinc-67 and the branching ratios in gallium-67 decay is given in Fig. 3. Although it is believed that the accuracy of the branching ratios is ample for radiation dosage calculations, these ratios are now being checked by independent methods.

⁽¹⁾K. Way, "Nuclear Data," NBS Circular 499.

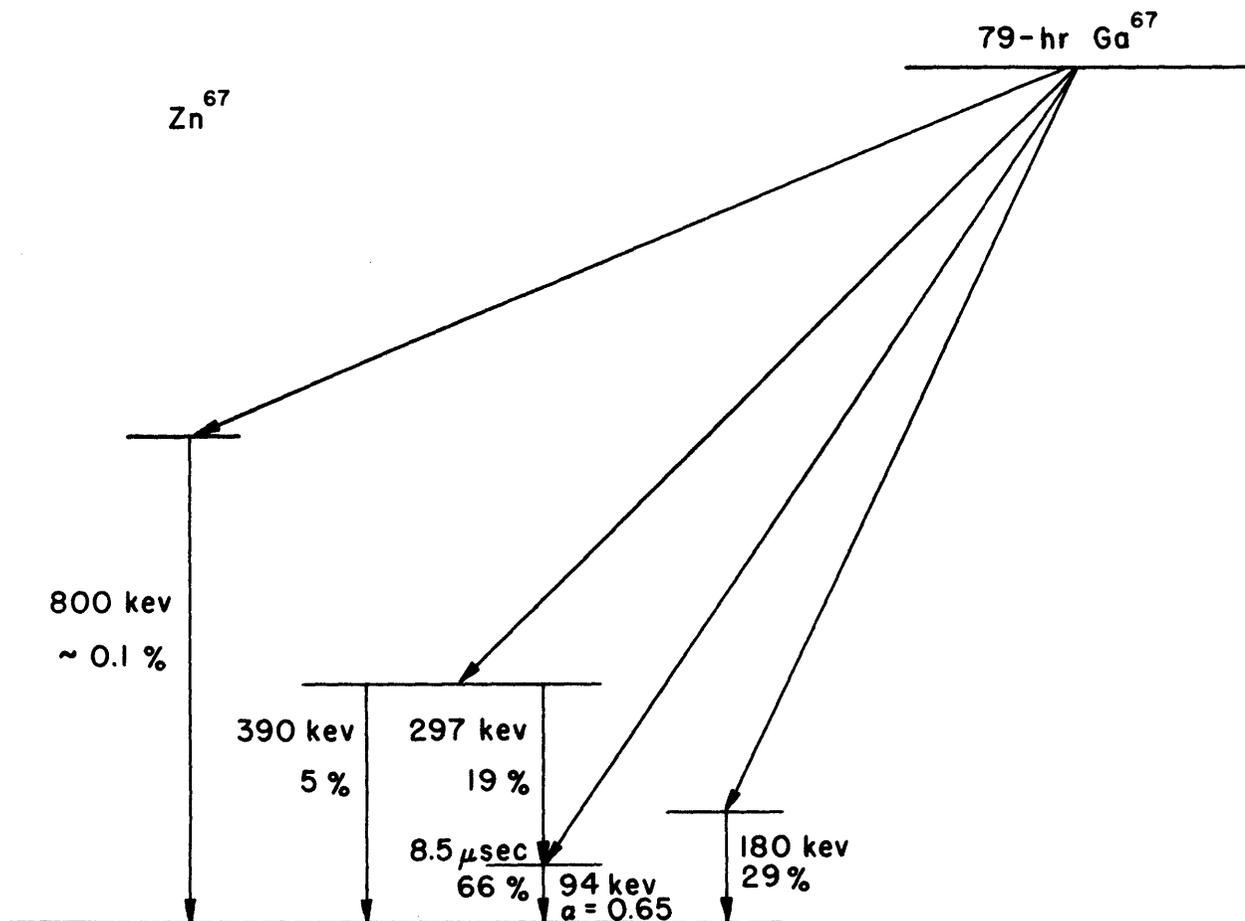


Fig. 3. Tentative Decay Scheme of Gallium-67.

The authors want to thank H. D. Bruner of the Medical Division of the Oak Ridge Institute of Nuclear Studies for suggesting this problem and for arranging the cyclotron bombardments and chemical separations. Thanks are also extended to E. Fairstein and F. M. Porter for help with the instruments used in this work:

FINE STRUCTURE IN THE FISSION-PRODUCT MASS-YIELD CURVE

G. W. Parker G. E. Creek

In conjunction with a current program involving collection and

purification of the radioactive fission gases, mass-spectrographic analyses of both the krypton and xenon fractions obtained were used to determine the relative fission yields. The results of the experiment generally confirm the xenon and krypton yields reported by Thode *et al.*,⁽²⁾ including the abnormally high yield at mass 134.

⁽²⁾H. G. Thode and R. L. Graham, "Mass-Spectrometer Investigation of the Isotopes of Xenon and Krypton Resulting from the Fission of Uranium-235 by Thermal Neutrons," *Can. J. Research*, 25A, 1-14 (1947); J. McNamara, C. B. Collins, and H. G. Thode, "The Fission Yield of Xenon-133 and Fine Structure in the Mass-Yield Curve," *Phys. Rev.*, 78, 129-34 (1950).

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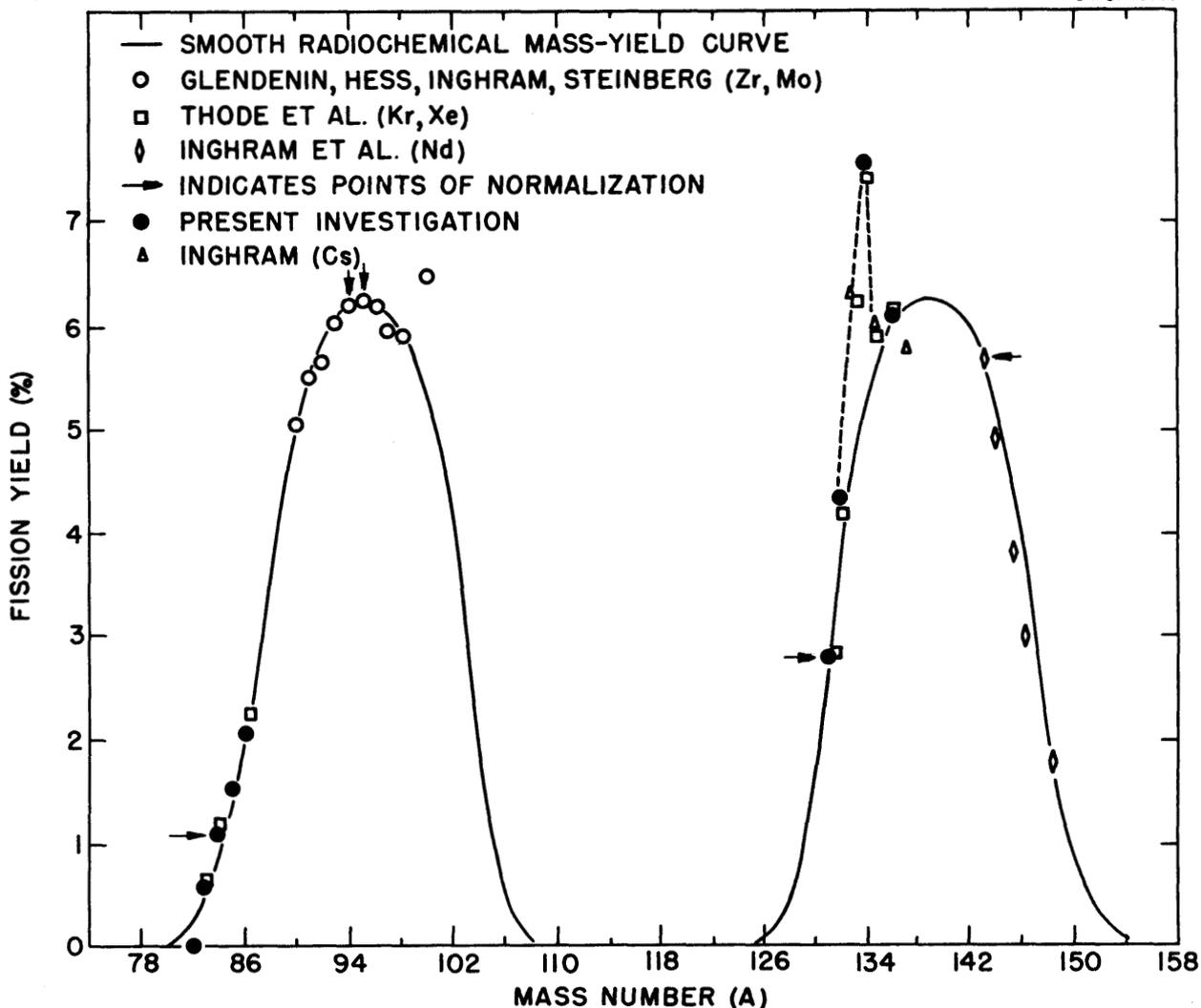


Fig. 4. Fine Structure of Mass-Spectrographic Fission-Product Yield Curve.

A renewed interest in the fission-product mass-yield curve recently culminated in a meeting⁽³⁾ of representatives from most of the large AEC and Canadian installations in which correlation and normalization of the accumulated mass-spectrographic and radiochemical yield data were attempted. Many of the implications of the problem were anticipated in a

paper by Glendenin *et al.*⁽⁴⁾ Figure 4, with some additional data from their investigation, is reproduced from the above report.

Among the factors proposed to explain the established deviation from the smooth symmetrical mass-yield curve is a preference for magic number configurations (82 neutrons, etc.)

⁽³⁾D. M. Wroughton to S. G. English, Letter, WAPD-C-36, August 8, 1951.

⁽⁴⁾L. E. Glendenin *et al.*, "Nuclear Structure in Fission" (to be published).

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in the fission process and delayed neutron and boil-off effects following fission.⁽⁵⁾ Since such effects have been established, it has become necessary to re-examine the individual members of each chain for accumulated yield. This is most reliably done with the mass spectrograph. For some of the moderately long-lived radioactive members, a correlation may be obtained by measuring ratios in both active and stable states, e.g., 5.3-d xenon-133 and stable cesium-133, and 8-d iodine-131 and stable xenon-131.

In this experiment, two Hanford uranium slugs (3550-g uranium and 2.04-g plutonium each), which had been irradiated in the "D" reactor from September 9, 1945 to October 21, 1946, were dissolved in hydrochloric acid in a closed glass system from which the krypton and xenon were swept by the large volume (120 moles) of hydrogen gas generated. The gas mixture was passed through drying traps into two 2-liter charcoal adsorbing beds at dry-ice temperature. Using a procedure suggested by Zeldes,⁽⁶⁾ the krypton was then eluted with hydrogen at room temperature into a smaller bed for sampling. The elution was repeated in a separate step while heating the large trap to the temperature of boiling water in order to elute the xenon. The mass-spectrographic analysis was furnished by C. R. Fultz and R. F. Hibbs of the Y-12 site. The observed mass ratios, expressed as percentages, were then recalculated as relative fission yields, using as a basis the smooth-curve value of 2.8% for xenon-131 and 1.09% for krypton-84. It was also necessary to use the reported value

of 33% of krypton-88 for the branching ratio in krypton-85 in order to make the corrections from the yield observed in 9.4-y krypton-85.

The yield of xenon-136 was calculated from the accepted value of 5.9% for xenon-135 and its probable cross section at the relatively low temperature of the Hanford reactor in 1945 and 1946. The authors are indebted to both J. A. Lane and R. W. Stoughton for assistance in this calculation. The resulting value of 6.1% is in good agreement with Thode's value of 6.14%. These values are included in Table 1.

The corresponding yields were then calculated for the krypton isotopes, and a decay and branching correction to the value for 9.4-y krypton-85 was made to determine the total yield of krypton at mass 85. The yield of the 4.3-h isomer reported⁽⁷⁾ (1.2%) was added to the observed 0.314% (Thode reported 0.316%) to give a total of 1.51% (Table 2).

A further experiment is under way to determine the absolute ratio of krypton to xenon mass spectrographically by isotopic dilution, thereby eliminating the uncertainty of relative yields and the need for two base values. A measurement of the cesium ratios in this same fission-product mixture should help to verify the cesium yields reported by Inghram (plotted in Fig. 4). Similar future studies of cesium have been planned by Glendenin and co-workers at Argonne and by Thode *et al.* in Canada.

⁽⁵⁾J. McNamara, C. B. Collins, and H. G. Thode, *loc. cit.*

⁽⁶⁾H. Zeldes, private communication.

⁽⁷⁾*Radiochemical Studies: The Fission Products*, NNES, Vol. IX, Book 2, p. 521 (New York: McGraw-Hill Book Co., 1951).

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Table 1

Fission Yields in the Mass 131 to 137 Region

MASS NO.	OBSERVED Xe (%) MASS-SPECTROGRAPHIC ANALYSIS	FISSION YIELD (%)			AVERAGE YIELD, CORRECTED TO 3.0% Xe ¹³¹ ***
		Xe ORNL DATA	Xe THODE'S DATA	Cs* INGHRAM'S DATA	
131	12.0	2.8(Base)	2.8(Base)		3.0(Base)
132	18.4	4.3	4.2		4.55
133	-	-	6.3	6.3(Base)	6.74
134	32.2	7.5	7.4		7.97
135	-	(5.9)	-	6.0	6.42
136	37.4	8.72 (136 + 135 n, γ) 6.1 (calc.)	6.14		6.55
137	-	-	-	5.7**	6.10

*Normalized by Glendenin *et al.*

**Probably not reliable.

***Suggested by recent data of Pappas and Coryell.

Table 2

Fission Yields in the Mass 83 to 86 Region

MASS NO.	OBSERVED Kr (%) MASS-SPECTROGRAPHIC ANALYSIS	FISSION YIELD (%)	
		ORNL DATA	THODE'S DATA
82	0.15	0.006	-
83	14.17	0.55	0.585
84	28.04	1.09 (Base)	1.09
85	5.23	0.314 (9.4-y) 1.51 (calc. total)	0.316 (9.4-y)
86	52.41	2.04	2.10

A recent announcement by Pappas and Coryell⁽⁸⁾ suggests that the

⁽⁸⁾A. C. Pappas, C. D. Coryell, *The Fission Yields Around the Neutron 82-Shell and the Effects of Closed Shell in Fission*, Presented at XVI Conference, International Union of Pure and Applied Chemistry, New York, September 1951.

yield for iodine-131 should be changed from 2.8 to 3.0%. Since this would "normalize" the yields in the principal xenon isotopes upward by about 0.5%, the corresponding values are also given in Table 1.

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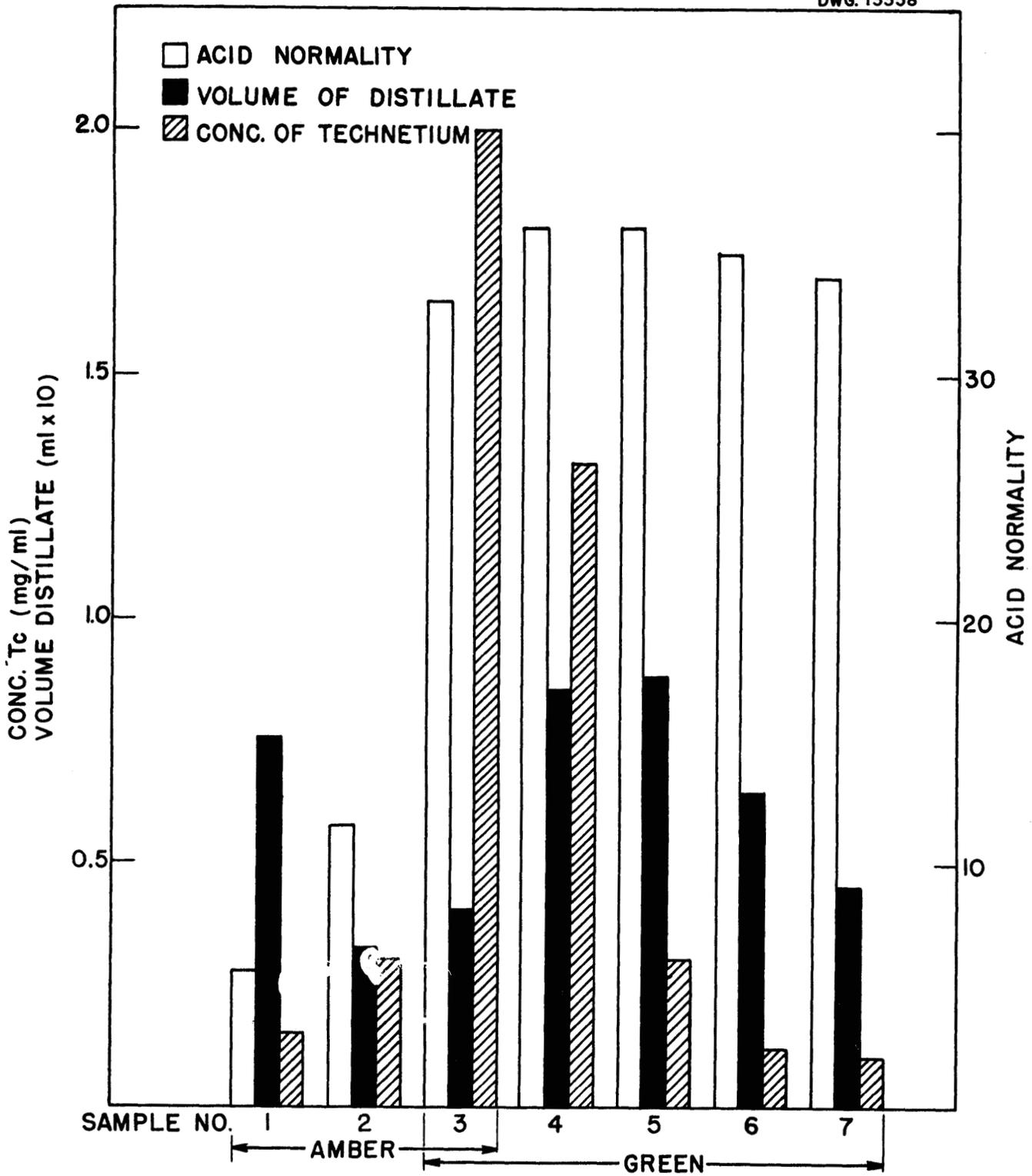


Fig. 5. Macro Distillation of Technetium (Tc_2O_7) with Sulfuric Acid.

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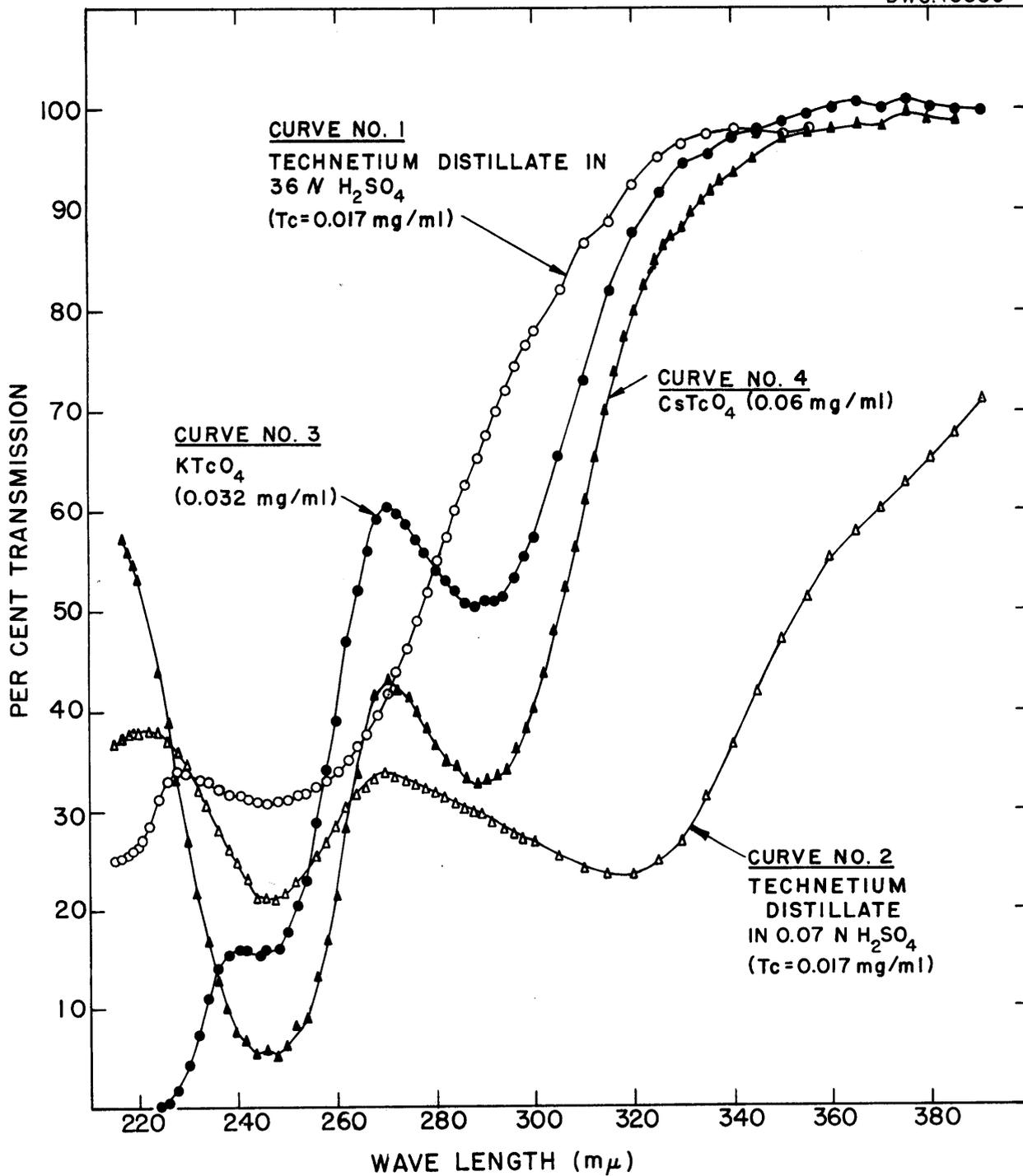


Fig. 6. Spectral Transmittancy Curves for Technetium (VII).

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DISTILLATION OF TECHNETIUM WITH SULFURIC ACID

W. J. Martin G. W. Parker

Final purification of technetium from crude process concentrates obtained from Chalk River metal wastes⁽⁹⁾ has been accomplished by the well-known method of sulfuric acid distillation. The tetraphenyl arsonium pertechnetate and tetraphenyl arsonium perchlorate-sulfuric acid solution is refluxed in a quartz still at 300°C until all organic material is destroyed. This step was formerly accomplished with the addition of catalytic selenium, however, the selenium is now being omitted. Some organic decomposition products are distilled as well as some perchloric acid. During this step the solution changes first to a jet black color and after the organic products are destroyed the solution is a green

color. The temperature is gradually increased until most of the sulfuric acid is distilled.

Figure 5 is a graphic reproduction of the average observations of a distillation of technetium with sulfuric acid. Seven samples from a distillation were collected in a sampling bulb and technetium concentration, sulfuric acid concentration, volume of distillate, and color were determined. Color intensities in the collected samples were roughly proportional to the concentration of technetium.

In Fig. 6 spectral transmittancy curves are shown for sample 4 (Fig. 5). By comparing a number of such absorption curves made over a range of sulfuric acid concentrations, it was concluded that the color variations observed as well as the intensity of one of the major spectrophotometric bands (2890 Å) in technetium distillate were due to hydration rather than to different oxidation states. The band at 2470 Å was relatively unaffected.

⁽⁹⁾G. W. Parker *et al.*, "New Hot Laboratory Facilities and Flow Plan for the Recovery of Fission Products and Neptunium from ORNL Redox Pilot Plant CR Wastes," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950*, ORNL-685, p. 62.

RADIO-ORGANIC CHEMISTRY

RADIATION, ANALYTICAL, AND
PREPARATIVE CHEMISTRYE. J. Dowling A. R. Jones
 W. J. Skraba

RADIATION CHEMISTRY

Experiments designed to determine the nature of the reactions of acetic acid induced by gamma radiation have continued.

Irradiation of a 0.01 *M* aqueous solution of acetic-1- C^{14} acid with a dose of approximately 10^7 r of gamma rays from a cobalt-60 source was found to cause decarboxylation to the extent of almost 30%. This percentage of radioactivity was found in the carbon dioxide fraction of the gaseous products. Negligible quantities of noncondensable gases such as methane or carbon monoxide were found. Similar experiments with acetic-2- C^{14} acid revealed only traces of activity in either the carbon dioxide or noncondensable gas fraction. The question as to the fate of the methyl fragment remaining after decarboxylation has therefore arisen. Tracer experiments in conjunction with paper chromatographic techniques have shown the absence (or presence in only trace quantities) of the possible oxidation products methanol and formaldehyde. Methods recently developed for their characterization⁽¹⁾ are now being employed to determine whether formic or propionic acid might be formed from the methyl fragment.

In addition to the formation of carbon dioxide by decarboxylation

three nonvolatile products were formed, two of which were identified as glycolic acid and succinic acid. The third constituent, though known to be an acid, is not positively identified.

When the experiments above were repeated with aqueous solutions 0.25 *M* in acetic acid the sole nonvolatile product found was succinic acid. Only 1% of the acetic acid was decarboxylated by a 10^7 -r dose. This represents, however, the decarboxylation of approximately the same number of acetic acid molecules as in the more dilute solution. Thus the rate of decarboxylation appears to be independent of acetic acid concentration in this concentration range.

Since the conversion yield to succinic acid is high and the decarboxylation reaction is relatively unimportant at this concentration, the use of this method for the synthesis of succinic-2,3- C_2^{14} acid from acetic-2- C^{14} acid is being investigated.

Experiments have been carried out to determine whether a carboxyl radical formed in the decarboxylation reaction can migrate intermolecularly before decomposition to carbon dioxide. Formic acid, known to form only carbon dioxide and hydrogen under the influence of gamma radiation, was chosen as the source of the carboxyl group. Acetic acid was chosen as the acceptor. A solution 0.01 *M* in formic- C^{14} acid and 0.01 *M* in non-radioactive acetic acid was irradiated. Paper chromatographic techniques revealed the presence of only one nonvolatile component, and this had an R_f value similar to that of the unknown material produced by the irradiation of 0.01 *M* aqueous acetic acid. Its identity is not yet established. That no reaction occurred

⁽¹⁾E. J. Dowling, A. R. Jones, and W. J. Skraba, "Radiation Chemistry," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951*, ORNL-1116.

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between radiation-activated carbon dioxide and acetic acid was shown by the irradiation of a 0.01 M aqueous solution of nonradioactive acetic acid containing dissolved carbon-14 dioxide. No nonvolatile radioactive compounds could be detected.

One irradiation of a benzene solution of labeled acetic acid (0.01 M) with a dose of 10^7 r produced no radioactive gases or nonvolatile products. Benzene which is unusually stable to radiation, probably because of the rapid internal conversion of absorbed energy, apparently does not readily transfer the energy of absorbed radiation to the solute.

One preliminary irradiation of a 0.01 M aqueous solution of valeric-1-C¹⁴ acid revealed only a trace of carbon dioxide from decarboxylation. The single nonvolatile product, identified tentatively from its paper chromatogram was α, α' -dipropylsuccinic acid, formed by dimerization of valeric acid.

ANALYTICAL CHEMISTRY

A method⁽²⁾ for the separation of the low molecular weight fatty acids by paper chromatography has recently been proposed. It was found to be unsatisfactory for our purposes since it gave insufficient difference in the R_f values, poor definition of the spots, and a considerable loss of acidic material by evaporation from the hydrolyzed ammonium salts.

These difficulties were eliminated by the use of diethylamine ($K_B = 1.26 \times 10^{-3}$) rather than ammonia ($K_B = 1.8 \times 10^{-5}$). Chromatography of radioactive formic, acetic, butyric, and valeric acids and the use of the

⁽²⁾E. P. Kennedy and H. A. Barker, "Paper Chromatography of Volatile Acids," *Anal. Chem.*, 23, 1033 (1951).

beta-ray densitometer enabled exact R_f values to be determined even though no adequate acid-base indicator has been found. These values will be given in a later report.

PREPARATIVE CHEMISTRY

Butyric-1-C¹⁴ acid (9.119 g, 103.6 mmoles, 21.1 mc) and valeric-1-C¹⁴ acid (8.832 g, 86.4 mmoles, 8.64 mc) were prepared by Grignard syntheses.

The preparation of valeric-2-C¹⁴ required the reduction of butyric-1-C¹⁴ acid to butanol-1-C¹⁴. High-pressure reduction of the cadmium-nickel salts in the presence of copper chromite catalyst⁽³⁾ gave only 58% yield, and the product was contaminated with butyl butyrate. Lithium aluminum hydride, however, reduced butyric acid to butanol almost quantitatively.

Attempts to prepare butyl iodide from butyl alcohol by the action of phosphorus and iodine⁽⁴⁾ led to many difficulties. Butyl bromide was, therefore, prepared in 80% yield by an adaptation of the procedure of Kamm and Marvel.⁽⁵⁾

ISOTOPE EFFECT STUDIES

MEASUREMENT OF THE CARBON-13 ISOTOPE EFFECT IN THE DEHYDRATION OF FORMIC ACID

A. J. Weinberger G. A. Ropp
O. K. Neville

The isotope effect in the dehydration of carbon-14-labeled formic acid in sulfuric acid solution has been previously determined by a flow

⁽³⁾P. T. Adams, R. E. Self, and B. M. Tolbert, *The Synthesis of Methanol-C¹⁴ and Methyl Iodine-C¹⁴ by High-Pressure Hydrogenation*, UCRL-1289.

⁽⁴⁾*Ibid.*

⁽⁵⁾O. Kamm and C. S. Marvel, *Organic Syntheses* (2d ed.; New York: John Wiley & Sons, 1947), Coll. Vol. I, p. 25.

method. The values determined for the difference between k_{12} and k_{14} for this reaction were $10.9 \pm 0.5\%$ at 0°C and $8.6 \pm 0.6\%$ at 25°C .

Preliminary work has now been done to determine the values for the carbon-13 isotope effect in this same reaction and if possible the activation energy difference. Since the flow method used previously was not applicable with a stable isotope, a system has been set up in which 20 successive samples of evolved carbon monoxide may be collected individually. Subsequently the carbon monoxide in each bulb may be burned to carbon dioxide over copper oxide and transferred to a sampler bulb for mass-spectrographic analysis. The formic acid used was of normal carbon-13 content and contained a tracer amount of formic- C^{14} acid. Since the amount of radioactive carbon dioxide was too small to be measured by the mass spectrograph but could be detected with the use of an ion chamber, it was possible to obtain a value for the carbon-14 isotope effect with the new method of measurement; this served as a check on the flow-system measurement.

On the basis of only one complete experiment the value of the carbon-14 isotope effect is found to be approximately the same at 0°C as reported previously. The value of the carbon-13 isotope effect for the sulfuric acid catalyzed dehydration of formic acid is about 5.76% at 0°C . This is approximately one-half of the value for formic- C^{14} acid.

ISOTOPE EFFECT IN THE UREASE-CATALYZED HYDROLYSIS OF UREA- C^{14}

D. Doherty* C. J. Collins

In 1948, Daniels and Meyerson⁽⁶⁾ reported a "reverse" isotope effect

*Member of the Biology Division.

in the urease-catalyzed hydrolysis of urea containing tracer amounts of urea- C^{14} . They reported that the carbon dioxide first evolved contained more carbon-14 dioxide than that evolved toward the end of the reaction.

Although "reverse" isotope effects are not unknown,⁽⁷⁾ the magnitude of the effect reported by Daniels and Meyerson prompted this reinvestigation.

Our data from 20 separate experiments have now failed to confirm the results of Daniels and Meyerson. They show, qualitatively at least, that the hydrolysis of carbon-14-labeled urea proceeds with a normal and not a "reverse" isotope effect, that is, the carbon dioxide first evolved contains less carbon-14 than that evolved toward the end of the reaction.

In this procedure, samples of 0.2 M urea- C^{14} (containing 0.176μ of $\text{C}^{14}/\text{mmole}$) in 0.25 M tris(hydroxymethylaminomethane)-phosphate buffer were treated with urease and allowed to react at 28°C with stirring for varying periods of time. The separate reaction mixtures were quenched with aqueous lactic acid solution, and the carbon dioxide samples evolved were measured manometrically. The gas samples were transferred to ion chambers and the carbon-14 content was determined.

Although experiments on any given day yield data through which a smooth

⁽⁶⁾A. L. Meyerson, *Summaries of Doctoral Dissertations* (Madison, Wisconsin: University of Wisconsin Press, 1950), 10, 465-67; A. L. Meyerson and F. Daniels, "Relative Rates of Hydrolysis of Urea Containing Carbon-12 and Carbon-14," *Science*, 108, 676 (1948).

⁽⁷⁾A. S. Roe and M. Hellman, private communication; H. Gilman, G. E. Dunn, and G. S. Hammond, "An Unusual Isotope Effect," *J. Am. Chem. Soc.*, 73, 4499-4500 (1951).

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curve may be drawn when total radioactivity evolved as carbon-14 dioxide is plotted against per cent of reaction, it has not been possible from day to day to obtain points that lie on the same curve. This may be due to different reaction inhibition periods, different degrees of deactivation of enzyme, or temperature effects on the enzyme solution prior to reaction.

The following are the data from one experiment:

Specific Activity as $\mu\text{c}/\text{mg C}$ in the C^{14}O_2 evolved	Per cent of reaction
0.0372	3.69
0.0416	3.98
0.0424	4.70
0.0454	10.1
0.0466	83.0

These are plotted in Fig. 7.

Further experiments are necessary to achieve standard conditions before this effect can be evaluated precisely. The present results, however, indicate qualitatively that a normal isotope effect occurs in the urea- C^{14} -urease reaction.

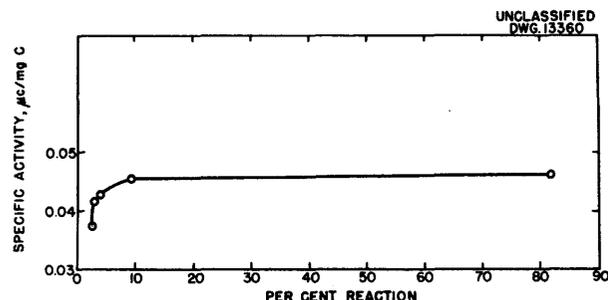


Fig. 7. A Plot of the Variations of Specific Activity with Per Cent Reaction in the Urea- C^{14} -Urease Hydrolysis.

ISOTOPE EFFECT IN THE CARBONATION OF ORGANOMETALLIC REAGENTS

D. E. Pearson* D. N. Hess
C. J. Collins

During a synthesis of chrysene-5,6- C^{14} , an isotope effect was indicated in the carbonation with carbon-14 dioxide of 9-benzo[*a*]fluorenesodium.⁽⁸⁾ The ratio of the observed molar specific activities of barium carbonate- C^{14} (657 $\mu\text{c}/\text{mmole}$) and the benzo[*a*]fluorene-9-carboxylic- C^{14} acid (595 $\mu\text{c}/\text{mmole}$) prepared from it was 1.10, indicating an isotope effect of the normal type.

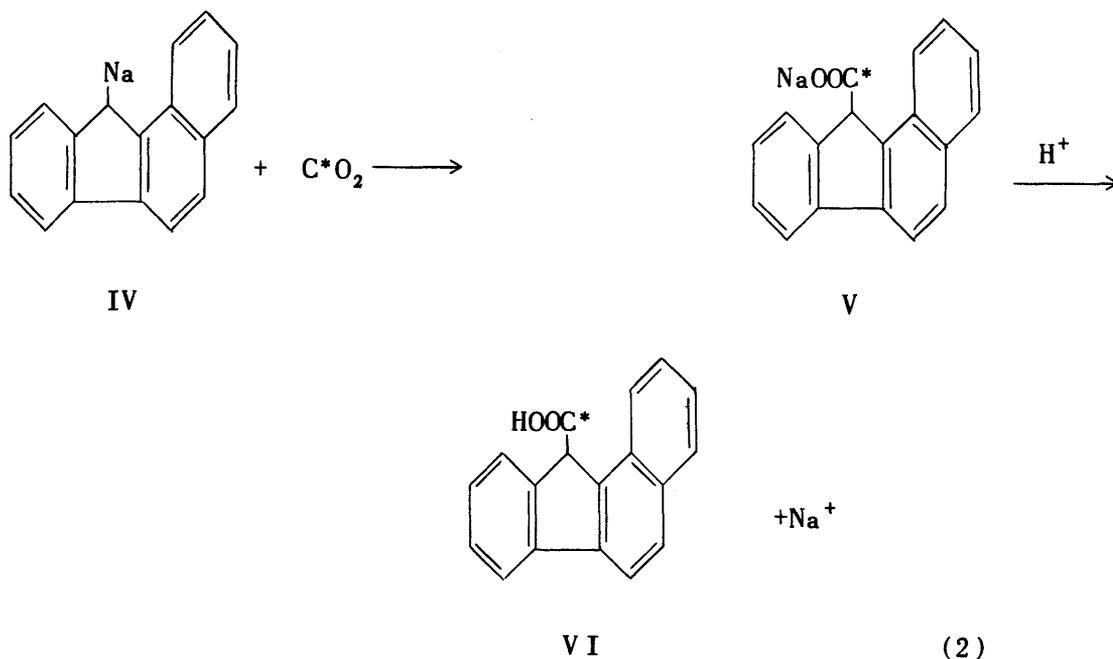
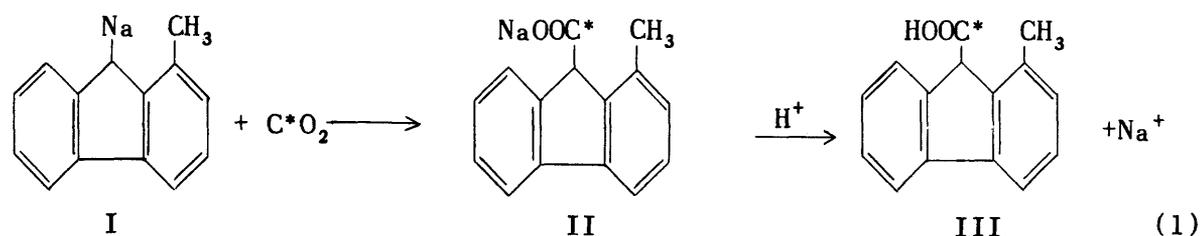
Owing to the known difficulties in obtaining chemically pure barium carbonate- C^{14} and to the attendant variations in observed specific activities of any given sample of barium carbonate- C^{14} , the data reported by Mayor and Collins⁽⁹⁾ cannot be taken as positive proof of an isotope effect. An experiment therefore was devised which circumvented the difficulties of the Mayor and Collins experiment. A liter bulb was filled to nearly atmospheric pressure with tracer-level carbon-14 dioxide. All carbonations were carried out with aliquots of this gas. The carbonations shown in the following equations were studied.

The molar radioactivity of the carbon-14 dioxide was established by performing reaction 1 with 1-methyl-9-fluorenesodium I in excess, and determining the radioactivity of the acid III so obtained. This

*Member of the Research Participation Program sponsored jointly by the Oak Ridge Institute of Nuclear Studies and Oak Ridge National Laboratory; permanent address, Vanderbilt University, Nashville, Tennessee.

⁽⁸⁾C. J. Collins and R. H. Mayor, "Synthesis of Chrysene-5,6- C^{14} ," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORNL-870, p. 53.

⁽⁹⁾*Ibid.*



molar specific activity was then checked by converting another aliquot of the carbon-14 dioxide to benzoic-7-C¹⁴ acid with an excess of phenylmagnesium bromide, and performing an assay on the benzoic acid obtained. No isotope effect should be expected in either of these reactions, since in either case all of the carbon-14 dioxide was converted to the appropriate acid. The data establishing the molar specific activity of the carbon-14 dioxide reservoir are given in Table 3.

Reactions 1 and 2 were then carried out with an excess of carbon-14 dioxide from the reservoir, and the acids III and VI were isolated and their molar radioactivities again determined. These data are given in Table 4.

From the data of Tables 3 and 4, it is apparent that the molar specific activity of the acid III is 3.24% less than the carbon-14 dioxide used in its preparation when a 5.3-fold excess of the latter reagent was used, and 1.83% less when a 1.5-fold excess was used. In the case of the one benzo[*a*]fluorene-9-carboxylic-C¹⁴ acid VI experiment (in which 1.5-fold excess of carbon-14 dioxide was used), the acid VI contained 4.35% less carbon-14 than the carbon-14 dioxide from which it was prepared.

Although these data are presumptive proof for an isotope effect in the carbonation of organometallic compounds, the magnitude of the measurable function of this effect is only two to three times the total

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Table 3

Radioactivity of Carbon-14 Dioxide Reservoir

	RADIOACTIVITY ($\mu\text{c}/\text{mmole}$)	
	WET COMBUSTION*	DRY COMBUSTION**
1-Methylfluorene-9-carboxylic- C^{14} acids	2.987 2.983 3.031 2.991	3.003
Benzoic-7- C^{14} acid	2.989	3.003
Average of all determinations	2.997 \pm 0.008 (standard deviation)	

*Determinations made by D. E. Pearson

**Determinations made by D. N. Hess

Table 4

Radioactivities of Acids III and VI When Prepared With an Excess of Carbon-14 Dioxide

	RADIOACTIVITY ($\mu\text{c}/\text{mmole}$)			
	5.3-FOLD EXCESS OF C^{14}O_2		1.5-FOLD EXCESS OF C^{14}O_2	
	WET COMBUSTION ^(a)	DRY COMBUSTION ^(b)	WET COMBUSTION ^(a)	DRY COMBUSTION ^(b)
1-Methylfluorene-9-carboxylic- C^{14} acid III	2.863 2.923 2.960 2.888 2.892	2.894	2.960 2.962 2.926 2.926 2.956 2.923	2.958
Average	2.903 \pm 0.014		2.944 \pm 0.006	
Benzo[a]fluorene-9-carboxylic- C^{14} acid VI				2.891 2.824
Average				2.857

^(a)Determinations made by D. E. Pearson

^(b)Determinations made by D. N. Hess

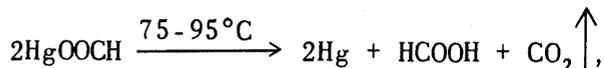
spread in the radioactivity determinations. Further experiments are necessary to rule out the possibility

of error in assigning these molar radioactivity differences to an isotope effect.

THERMAL DECOMPOSITION OF MERCUROUS FORMATE-C¹⁴

V. F. Raaen G. A. Ropp

Because of an interest in the isotope effect in the reactions of formic acid⁽¹⁰⁾ and formates, the recently studied decomposition of mercurous formate,⁽¹¹⁾



was examined for isotope fractionation using carbon-14-labeled mercurous formate. It was thought possible that the distribution of the carbon between the two products, liquid formic acid and gaseous carbon dioxide, might give rise to an isotope effect of unusual magnitude which could be easily followed as a variation of the carbon dioxide specific activity with per cent reaction.

An isotope effect was positively demonstrated by the increase of the carbon dioxide specific with time as the reaction proceeded. However the reaction did not obey the simple first-order rate law as had been reported,⁽¹²⁾ and therefore the ratio, k_{14}/k_{12} , of the carbon-14 rate constant to the carbon-12 rate constant could not be evaluated.

Experimental

Preparation of mercurous formate-C¹⁴. By the method of Miller and Murphy⁽¹³⁾ mercurous formate-C¹⁴ was

⁽¹⁰⁾G. A. Ropp, A. J. Weinberger, and O. K. Neville, "Isotope Effect in Decomposition of Formic Acid-C¹⁴," *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1950*, ORNL-1036, p. 47.

⁽¹¹⁾G. A. Miller and G. W. Murphy, "Kinetics of the Decomposition of Solid Mercurous Formate," *J. Am. Chem. Soc.*, 73, 1871 (1951).

⁽¹²⁾*Ibid.*

⁽¹³⁾*Ibid.*

precipitated at low temperatures from a solution of sodium formate-C¹⁴ that had a specific activity of about 10 $\mu\text{c}/\text{mg}$. Although all precautions were taken in purifying and handling the solid, some samples darkened slightly before use.

Demonstration of the isotope fractionation in the carbon-14 dioxide. Labeled mercurous formate (10 mmoles, 2.50 g) was permitted to decompose over an 8-hr period in a 25-ml reaction bulb at 70 to 75°C. The bulb was continuously swept with nitrogen, which was previously passed through drierite-ascarite mixture and through aqueous potassium hydroxide to saturate the gas with water. Gases leaving the reaction bulb were passed through a series of nine absorption bottles equipped with fritted bubble tubes. The bottles were filled with saturated aqueous barium hydroxide. When the barium hydroxide in the first bottle was exhausted, that bottle was by-passed and the gas was passed through the succeeding eight bottles. In this manner each of the first eight bottles was in turn by-passed to prevent possible exchange of the carbon dioxide with previously precipitated barium carbonate. When the reaction was complete, the barium carbonate samples were collected, washed thoroughly with water by decantation, filtered, and dried 15 hr at 120°C in a stream of nitrogen. The washing and drying procedures were critical in obtaining reproducible assays of the barium carbonate-C¹⁴. The barium carbonate-C¹⁴ samples were weighed. Collectively they represented 91% recovery of carbon dioxide. Weighed samples were decomposed with 85% phosphoric acid and each carbon-14 dioxide sample released was collected in a stainless steel ion chamber for radiochemical assay. Table 5 presents the results of these assays.

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Table 5

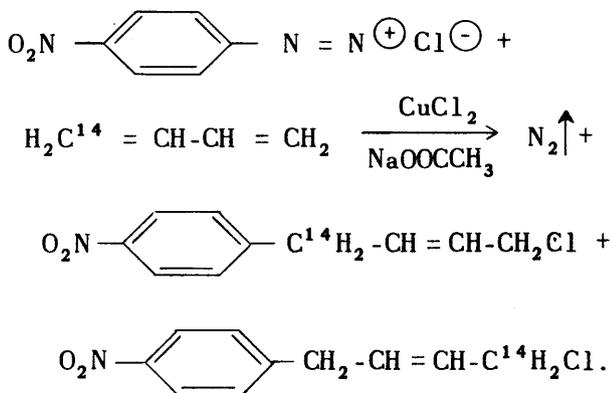
Isotope Fractionation of Carbon-14 Dioxide in the
Decomposition of Mercurous Formate-C¹⁴

SAMPLE BaC ¹⁴ O ₃	PER CENT OF REACTION REPRESENTED	SPECIFIC ACTIVITY (μc/mg × 10 ²)
1	5	9.98
2	5	9.99
3	5	10.03
4	15	-
5	36	10.38
6	16	10.57
7	9	11.17

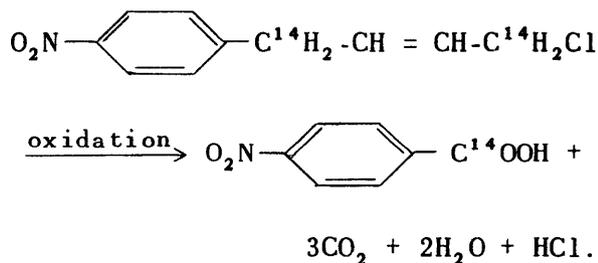
EXAMINATION OF A MEERWEIN REACTION FOR AN ISOTOPE EFFECT

V. F. Raaen G. A. Ropp

The reaction of *p*-nitrophenyldiazonium chloride with butadiene in the presence of cupric chloride and sodium acetate, which is an example of a Meerwein reaction,⁽¹⁴⁾ was examined for an isotope effect using 1,3-butadiene-1-C¹⁴. In the event of an isotope effect the product, 1-chloro-4-(*p*-nitrophenyl)butene-2, could have different concentrations of carbon-14 in the alpha and delta positions to the ring. In the absence of any isotope effect these two positions would have identical concentrations of carbon-14:



Furthermore, in the absence of any isotope effect the alpha position to the ring would have one-half the carbon-14 concentration of the entire molecule; this relationship would not hold in the event of an isotope effect. For these reasons the carbon-14-labeled product was first radiochemically assayed as such, and then was degraded to *p*-nitrobenzoic acid which was also assayed:

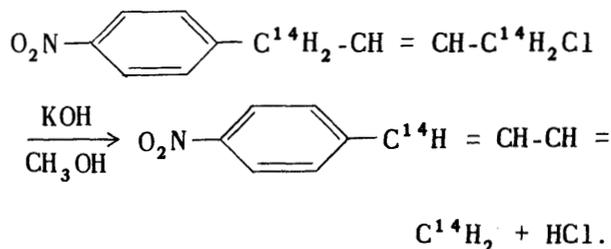


The absence of an isotope effect was shown by the fact that the specific activity of the *p*-nitrobenzoic acid was one-half that of the 1-chloro-4-(*p*-nitrophenyl)-butene-2, within experimental error. This meant that the rate of attack on the labeled end of butadiene molecule was the same as the rate of attack on the unlabeled end.

Because the product 1-chloro-4-(*p*-nitrophenyl)-butene-2 is a liquid, its specific-activity determination was most readily accomplished after

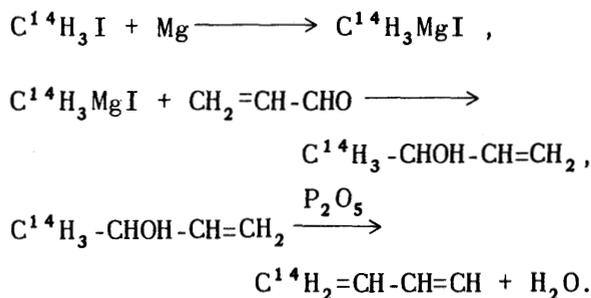
⁽¹⁴⁾E. C. Coyner and G. A. Ropp, "Preparation of 1-(*p*-nitrophenyl)-1,5-butadiene," *J. Am. Chem. Soc.*, 70, 2283-4 (1948).

dehydrohalogenation⁽¹⁵⁾ to the crystalline, easily purified diene, 1-*p*-nitrophenylbutadiene-1,3.



This procedure, however, did not complicate the picture since the dehydrohalogenation was practically quantitative, and therefore could not introduce an isotope effect of its own to cause a difference in specific activity between the chloride and the diene.

Butadiene, unsymmetrically labeled with carbon-14, was synthesized according to the following equations:



Experimental

Synthesis of 1,3-butadiene-1-C¹⁴. By a conventional Grignard addition, methyl-C¹⁴ vinyl carbinol was prepared by addition of methyl-C¹⁴ iodide to acrolein. From methyl-C¹⁴ vinyl carbinol, 1,3-butadiene-1-C¹⁴ was prepared in 33% yield by heating to 300°C in nitrogen atmosphere over phosphorus pentoxide. The diene had a specific activity of about 1 μc/mole.

Meerwein reaction of 1,3-butadiene-1-C¹⁴. The reaction of *p*-nitrophenyl-

diazonium chloride with 1,3-butadiene-1-C¹⁴ and the dehydrohalogenation of the product, 1-chloro-4-(*p*-nitrophenyl)-butene-2, were carried out as described by Coyner and Ropp.⁽¹⁶⁾ 1-*p*-Nitrophenylbutadiene-1,3 was obtained (mp 82 to 83°C).

Oxidation of 1-chloro-4-(p-nitrophenyl)-butene-2. Two grams of the oily distilled chloride was added to a cooled solution of 15 g of sodium dichromate, 50 ml of water, and 15 ml of cp sulfuric acid. The mixture was boiled 3 hr and poured onto ice. The *p*-nitrobenzoic acid was extracted with sodium bicarbonate solution, and on acidification about 1 g (63%), mp 235 to 237°C, was recovered.

After both the 1-*p*-nitrophenyl-1,3-butadiene and the *p*-nitrobenzoic acid were purified by recrystallization, both were assayed radiochemically. The specific activity of the *p*-nitrobenzoic acid when doubled was 1.1% greater than the specific activity of the 1-*p*-nitrophenyl-1,3-butadiene, a difference probably due to experimental error. The following figures were obtained:

Acid (μc/mole),	1.345, 1.360
Diene (μc/mole),	2.645, 2.704, 2.635

EXAMINATION OF A DIELS-ALDER REACTION FOR AN ISOTOPE EFFECT

G. A. Ropp V. F. Raaen

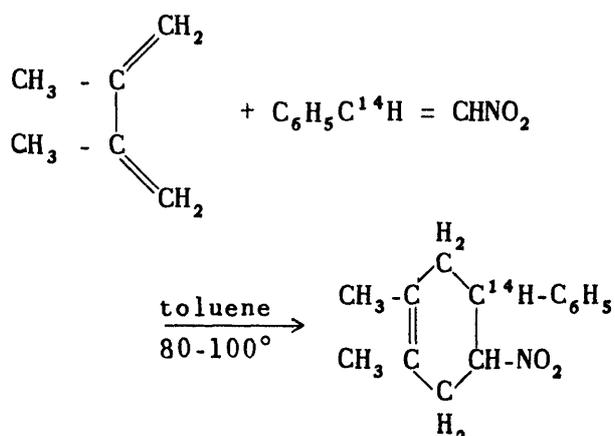
The belief that there might be a measurable isotope effect in a simple addition reaction led to a study of the addition of 2,3-dimethylbutadiene to β-nitrostyrene labeled with carbon-14 in the alpha position to the ring. This reaction⁽¹⁷⁾ proceeds at low temperatures and gives high yields of an easily purified adduct.

(16) *Ibid.*

(17) C. F. H. Allen, A. Bell, and J. W. Gates, Jr., "The Diene Synthesis with β-Nitrostyrene," *J. Org. Chem.*, 8, 373-9 (1943).

(15) *Ibid.*

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To test for an isotope effect, the reaction of 2,3-dimethylbutadiene with β -nitrostyrene- α - C^{14} was permitted to go to completion, and the product was isolated and its specific activity measured.

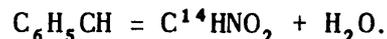
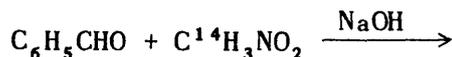
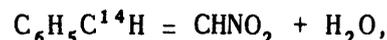
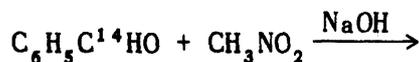
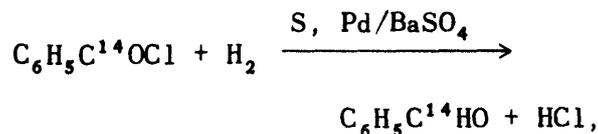
When the reaction was repeated, but stopped at approximately 30% completion, the isolated product had essentially the same specific activity as in the first reaction, indicating no isotope effect. The reaction is being repeated, stopping at smaller percentage reactions, to improve the sensitivity of the method. A similar study with β -nitrostyrene- β - C^{14} is also in progress.

Since certain Diels-Alder reactions are reversible,⁽¹⁸⁾ it was of interest to demonstrate that the adduct formed from 2,3-dimethylbutadiene and β -nitrostyrene did not decompose even at 130°C , i.e., 50° above the temperature at which the reactants combined to form the adduct. Since the reverse reaction was shown not to occur at a measurable rate, the possibility was eliminated that an isotope effect might have been present but masked by a rapid exchange of the adduct with the dienophile. This proof of irreversibility was effected by heating β -nitrostyrene- α - C^{14} with a portion of

⁽¹⁸⁾M. C. Kloetzel, "The Diels-Adler Reaction with Maleic Anhydride," *Organic Reactions* (New York: John Wiley & Sons, 1948), IV, 9.

the unlabeled adduct for 24 hr at 130°C , isolating the adduct, and showing that it contained only background activity.

The following reactions were used in the synthesis of the labeled dienophiles:



Experimental

Synthesis of dienophiles. Conventional procedures were used in synthesizing labeled benzaldehyde,⁽¹⁹⁾ nitromethane,⁽²⁰⁾ and the β -nitrostyrenes⁽²¹⁾ having specific activities of 1 to 5 $\mu\text{c}/\text{mmole}$.

Diels-Alder reactions. In a typical run in which the reaction was carried to completion, 30 mmoles of 2,3-dimethylbutadiene, 20 mmoles of β -nitrostyrene, and 30 mmoles of toluene were stirred at reflux temperature. The course of the reaction in this case, as in those where the reaction was stopped before completion, was followed by plotting the

⁽¹⁹⁾E. Mosettig and R. Mazingo, "The Rosenmund Reduction of Acid Chloride to Alcohols," *ibid.*, p. 362.

⁽²⁰⁾J. C. Sowden, "The Condensation of C^{14} -nitromethane with D-arabinose: Preparation of 1-C^{14} -D-glucose and 1-C^{14} -D-mannose," *J. Biol. Chem.*, 180, 55-8 (1949).

⁽²¹⁾A. H. Blatt, *Organic Syntheses* (2d ed.; New York: John Wiley & Sons, 1946), Coll. Vol. I, p. 413.

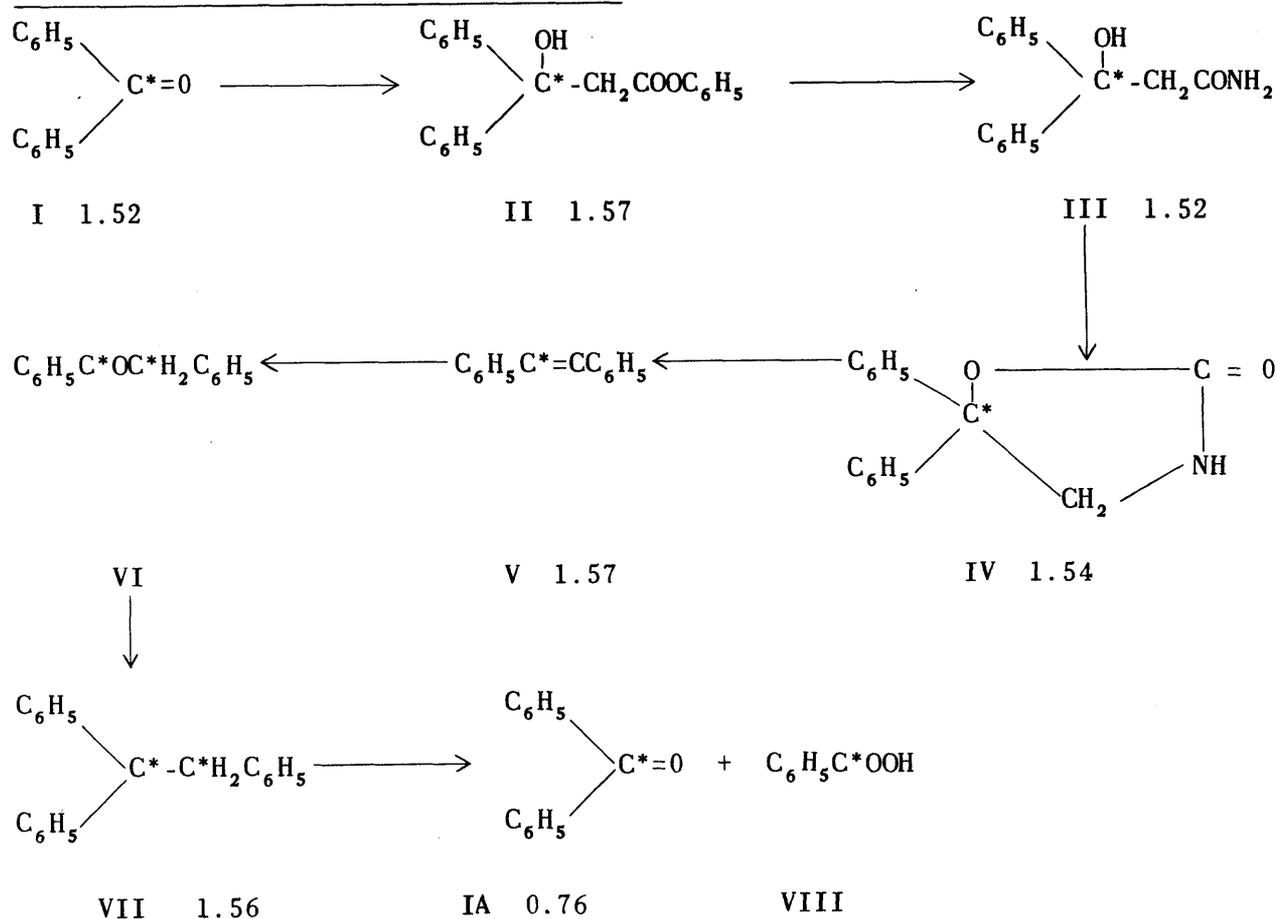
equilibrium temperature of the boiling solution against time. This temperature rose steadily and the per cent completion was indicated approximately by the liquid temperature as the more volatile diene was consumed and the solution became more concentrated. In the case of the reaction, which was carried to approximately 30% completion, the heating was stopped when the temperature rose from 85 to 93.5°C. The excess diene and the toluene were distilled off *in vacuo* and pure adduct was separated from unreacted dienophile in the residue by fractional extraction with ethanol, recrystallization from aqueous ethanol, and vacuum sublimation. Recovered adduct (mp 91.5 to

92.5°C) had a specific activity of 1.29 $\mu\text{c}/\text{mg}$ as compared with 1.30 $\mu\text{c}/\text{mg}$ for adduct recovered after complete reaction.

ADDITION OF WATER TO DIPHENYL(ACETYLENE-1-C¹⁴)

J. G. Burr, Jr.

The possibly unsymmetrical addition of the elements of water across the C¹²=C¹⁴ triple bond of diphenyl (acetylene-1-C¹⁴) has been investigated. This substance was synthesized by the procedure of Newman and Kutner.⁽²²⁾ The series of reactions employed in the synthesis, hydration, and degradation of the hydrated acetylene follows:



(22) M. S. Newman and A. Kutner, "New Reactions Involving Alkaline Treatment of 3-Nitroso-2-oxazolidones," *J. Am. Chem. Soc.*, 73, 4199 (1951).

The arabic numerals represent the radioactivities in $\mu\text{c}/\text{mmole}$. The average of ten determinations upon

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the compounds I through VII was $1.55 \pm 0.02 \mu\text{c}$ of C^{14} /mmole. When this is compared with the value of $1.52 \pm 0.02 \mu\text{c}$ of C^{14} /mmole, which is twice the observed activity of the degradation product, I, it is apparent that if there is any isotope effect in the hydration of diphenylacetylene its measurable function must be of the order of 1 to 2%. The results of the assays upon the other degradation product, benzoic acid VIII, could not be applied to this study, since the low value obtained, $0.66 \mu\text{c}$ of C^{14} /mmole, indicated that the benzoic acid must have been diluted during the oxidation of VII with benzoic acid from some inactive source—probably from impurities present in the crude carbinol VII used for the oxidation.

Experimental

Diphenyl ketone-C¹⁴ I. Thirty-five grams of aluminum chloride was added portionwise to a mixture of 56 g benzene, 60 ml of carbon disulfide, 28.1 g of benzoyl chloride, and 50.1 mg of benzoic acid containing about 1 mc of carbon-14. After stirring overnight, the mixture was hydrolyzed, and the product processed and then distilled. The product was 26.34 g (72%). The still was recharged with 21.33 g of inactive benzophenone, of which 19.70 g was recovered in the distillate, making a total of 46.04 g (253 mmole) of crystalline benzophenone. A portion of this was converted to the oxime, mp 141°C , which was recrystallized for assay. The assay showed 1.50, 1.53 μc of C^{14} /mmole.

Ethyl 3-hydroxy-3,3-diphenylpropionate-3-C¹⁴ II. This was prepared by the procedure of Rupe and Busolt,⁽²³⁾

⁽²³⁾H. Rupe and E. Busolt, " β -Phenyl-zimtsäure (β,β -Diphenyl-acrylsäure)," *Ber.*, 40, 4537 (1907).

in essentially quantitative yield as a solid, which after crystallization melted at 85 to 86°C . It contained 1.56, 1.58 μc of C^{14} /mmole.

3-Hydroxy-3,3-diphenylpropionic acid-3-C¹⁴ hydrazide III. This was prepared by refluxing the ester (13.5 g) with a mixture of 10 ml of 95% hydrazine hydrate and 25 ml of ethanol for 3 hr. The yield was 16 g of colorless solid, which after crystallization from benzene melted at 130°C and contained 1.52 μc of C^{14} /mmole.

5,5-Diphenyl-2-oxazolidone-4-C¹⁴ IV. A solution of the hydrazide (7.2 g) in 60 ml of 6 N hydrochloric acid was treated, with stirring, with a solution of 2.1 g of sodium nitrite in 15 ml of water. The suspension of white solid that formed was heated on the steam bath until cessation of gas evolution, and the resulting clear yellow solution was cooled and diluted with water. The pale yellow crystalline solid that formed was filtered (4.1 g, mp 196 to 198°C) and crystallized from ethanol to give colorless crystals melting at 200°C and containing 1.56, 1.52 μc of C^{14} /mmole.

Diphenyl(acetylene-1-C₁¹⁴) V. The above oxazolidone was converted through the nitroso compound to the acetylene by the procedure described by Newman and Kutner.⁽²⁴⁾ The acetylene was obtained in 60% yield as a pale cream solid (mp 52 to 55°C). Recrystallization from alcohol water gave colorless needles melting at 56 to 57°C and containing 1.59, 1.56 μc of C^{14} /mmole.

Benzyl phenyl ketone-C¹⁴ VI. A portion of the above acetylene (0.50 g) was warmed with a mixture of 5 ml concentrated sulfuric acid and 15 ml

⁽²⁴⁾*Loc. cit.*

of acetic acid until a clear solution resulted (about 1 hr), and then a few crystals of mercuric chloride were added and warming continued for a few minutes. The solution was poured into water, and the pale yellow precipitate was filtered and air-dried. It weighed 500 mg and melted at 51 to 52°C. The mixture melting point of this with authentic desoxybenzoin (mp 51 to 52°C) showed no depression, but the mixture melting point with diphenylacetylene (mp 56 to 57°C) was 35 to 45°C.

Benzylidiphenyl(carbinol-C¹⁴) VII. The above product was added to the Grignard solution prepared from 3 g of bromobenzene and 0.5 g of magnesium, and the resulting turbid suspension was stirred overnight. Hydrolysis and crystallization of the product from hexane gave 480 mg of nearly colorless needles that melted at 88°C and contained 1.56 μc of C¹⁴/mmole.

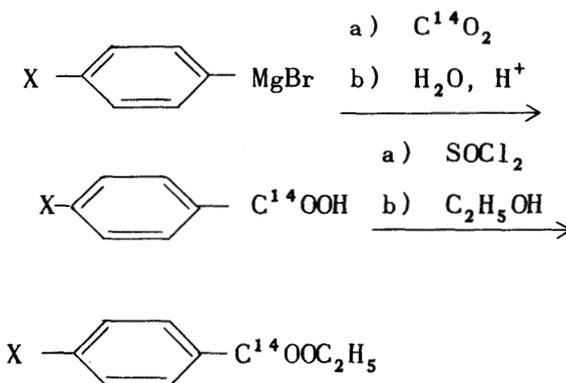
Oxidation of benzylaiphenyl(carbinol-C¹⁴). After about 100 mg of the above material had been reserved for analysis, the remaining 380 mg plus the entire crude Grignard adduct was heated for 1 hr on the steam bath with a solution of 0.5 g of chromic oxide in 10 ml of acetic acid. The dark green solution was poured into water, and the water solution was ether extracted. This ether extract was shaken with 1 N sodium hydroxide and water, and then dried and evaporated. The residual darkish oil was heated with hydroxylamine hydrochloride, pyridine, and ethanol to give, after crystallization from dilute ethanol, 150 mg of benzophenone oxime whose melting point and mixture melting point with authentic oxime (mp 141°C) was 141°C. It contained 0.756, 0.758, 0.763 μc of C¹⁴/mmole. The alkaline extract obtained above was acidified and ether extracted. The darkish oil obtained from the ether

was treated with a large excess of thionyl chloride, and the solution was heated under vacuum to remove excess thionyl chloride and any acetyl chloride. The residue from this was dissolved in benzene and treated with excess aniline. The benzene solution, after washing with water and drying, was evaporated and the residual solid crystallized from benzene. The benzanilide was thus obtained as colorless plates, which melted at 161°C and contained 0.690, 0.656, 0.660, and 0.676 μc of C¹⁴/mmole. This substance was apparently diluted nonradioactive benzoic acid whose probable source was an impurity in the crude carbinol used for the oxidation.

COMPARISON OF THE ISOTOPE EFFECTS IN THE ALKALINE HYDROLYSIS OF FOUR *PARA*-SUBSTITUTED ETHYL BENZOATES LABELED IN THE CARBONYL GROUP

G. A. Ropp, V. F. Raaen

In preparation for a systematic study of the effect of *para*-substituents on the magnitude of the isotope effect in the hydrolysis of ethyl benzoates, four carboxyl-labeled esters have been prepared according to the following reactions:

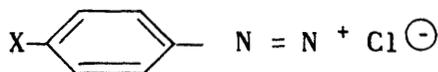


(1) X = -CH₃

(2) X = -OCH₃

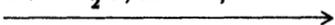
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(3) X = -Cl

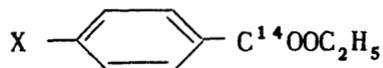
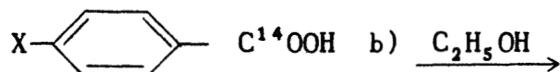


a) $\text{KCu}(\text{C}^{14}\text{N})_2$

b) $\text{H}_2\text{O}, \text{OH}^(-), \text{H}^(+)$



a) SOCl_2



(4) X = -NO₂

The Grignard carbonations (1, 2, and 3) were carried out according to standard procedures as described in *Organic Syntheses*.⁽²⁵⁾ The yields based on labeled carbon dioxide were nearly quantitative. As intermediates in the preparation of carbon-14-labeled *p*-nitrobenzoic acid (4), carbon-14-labeled cuprous cyanide, and then carbon-14-labeled potassium cuprous cyanide were prepared according to the procedures of Barber.⁽²⁶⁾ All four ethyl esters were synthesized in high yield from the corresponding acids via the acid chlorides prepared using thionyl chloride.

It is planned to measure k_{14}/k_{12} , the ratio of the hydrolysis rate constant of carbon-14-labeled ester to that of the unlabeled ester, for each of the four *p*-substituted esters using a modification of the method

⁽²⁵⁾ *Loc. cit.*

⁽²⁶⁾ H. J. Barber, "Cuprous Cyanide—Its Preparation and Use," *J. Chem. Soc.*, 79 (1943).

of Stevens and Attree.⁽²⁷⁾ This series of reactions was chosen for study because the difference in reaction rates within the series has been shown to result entirely from difference in energy of activation, the A factor in the Arrhenius equation remaining essentially constant.⁽²⁸⁾ The carbon-14 isotope effect on reaction rates has been assumed to result principally from alteration⁽²⁹⁾ of the activation energy. Hence the present study may indicate whether the isotope effect increases, decreases, or remains unchanged in going from a reaction of a given activation energy to one of higher activation energy, while other influences on reaction rate are held constant.

STUDIES ON THE MECHANISMS OF ORGANIC REACTIONS

ISOTOPE-EXCHANGE REACTIONS INVOLVING THE CARBON-CARBON BOND

C. D. Douglass* O. K. Neville

Experiments to determine the reversibility of the Friedel-Crafts

*Oak Ridge Institute of Nuclear Studies Graduate Fellow from the University of Oklahoma, Norman, Oklahoma.

⁽²⁷⁾ W. H. Stevens and R. W. Attree, "Effect on Reaction Rates Caused by the Substitution of Carbon-14 for Carbon-12. I. Alkaline Hydrolysis of Carboxyl-labeled Ethyl Benzoate," *Can. J. Research*, 27B, 807-12 (1949).

⁽²⁸⁾ C. K. Ingold and W. S. Nathan, "Mechanism of and Constitutional Factors Controlling the Hydrolysis of Carboxylic Esters. VIII. Energies Associated with Induced Polar Effects in the Hydrolysis of Substituted Benzoic Ester," *J. Chem. Soc.*, 1936, 222-5; D. P. Evans, J. J. Gordon, and H. B. Watson, "Ortho-effect. III. Alkaline Hydrolysis of Benzoic Esters," *ibid.*, 1937, 1430-2; "Influence of Alkyl Groups Upon Reaction Velocities in Solutions. III. The Alkaline Hydrolysis of Saturated Aliphatic Esters," *ibid.*, 1938, 1439-44.

⁽²⁹⁾ A. A. Bothner-By, L. Friedman, and J. Bigeleisen, "The Use of Tracers in Organic Reaction Mechanism Studies," *BNL Conference Report*, January 19-20, 1950, p. 40.

acylation reaction by isotopic exchange are nearly complete. Previously reported attempts⁽³⁰⁾ to effect the exchange of acetyl chloride with acetophenone and benzoyl chloride with benzophenone have been extended to other substituted aromatic systems. Neither compounds with extreme ring activation, such as resacetophenone and acetophloroglucinol, nor those with extreme ring deactivation, such as trinitrobenzophenone, have been found to exchange with the appropriate acyl chloride under the influence of Friedel-Crafts acid catalysts. Table 6 shows the conditions used in these studies. The conclusion has been reached, therefore, that in general such reactions are not formed by reversible processes. This in no way rules out the possibility that certain examples might be found that are reversible.

This exchange technique has now been turned to the study of base-catalyzed condensations, all of which may be classified as "aldol" condensations. An example of the reaction type is the condensation of benzaldehyde with acetophenone in the presence of concentrated aqueous alkali to form benzalacetophenone (chalcone) II.

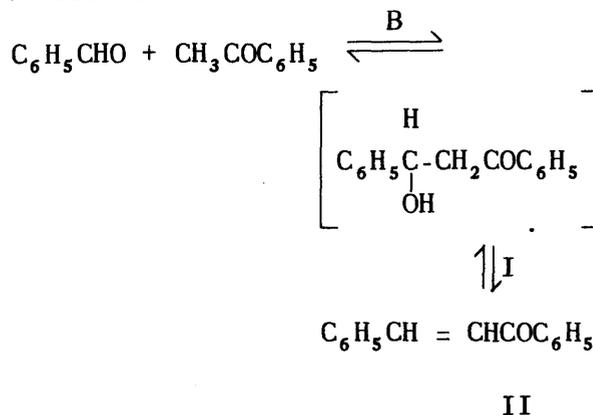


Table 6

Conditions Used in Studies of the Reversibility of the Friedel-Crafts Acylation Reaction*

KETONE	ISOTOPIC ACID OR ACID CHLORIDE	CATALYST	MOLAR PROPORTION OF CATALYST	SOLVENT	TEMPERATURE	TIME
<i>p</i> -CH ₃ OC ₆ H ₄ COCH ₃	CH ₃ COC1	AlCl ₃	3	CS ₂	Room	2 days
<i>o</i> -HOC ₆ H ₄ COCH ₃	CH ₃ COC1	AlCl ₃	3	CS ₂	Room	8 days
2, 4, 6-(HO) ₃ C ₆ H ₂ -COCH ₃	CH ₃ COC1	AlCl ₃	3	Cl ₂ CHCHCl ₂	Room	6 days
2, 4-(HO) ₂ C ₆ H ₃ -COCH ₃	CH ₃ COOH	HBr	none	-	Room	12 hr
C ₆ H ₅ COC ₆ H ₅	C ₆ H ₅ COC1	Conc. H ₂ SO ₄	Catalytic amount	none	120°C	2 days
2, 4, 6-(NO ₂) ₃ C ₆ H ₂ COC ₆ H ₅	C ₆ H ₅ COC1	AlCl ₃	3	Cl ₂ CHCHCl ₂	Room	1 day

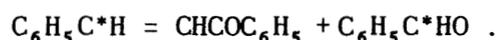
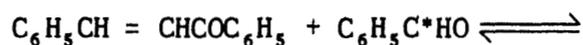
*No evidence of exchange was found in any of the reactions.

⁽³⁰⁾C. D. Douglass and O. K. Neville, "Isotope-Exchange Reactions Involving the Carbon-Carbon Bond," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951*, ORNL-1116.

Although such reactions frequently terminate with the aldol intermediate as represented by I, in many cases

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the final product isolated is an α,β -unsaturated carbonyl compound II formed presumably by dehydration of the aldol I. In some cases, either product may be isolated at will, depending on the reaction conditions. Although condensation to give the aldol intermediate is well recognized as a reversible reaction, the terminating dehydration step is considered usually to be irreversible under the conditions of the reaction. This reaction and others similar to it have now been studied by the exchange technique



The isolation of carbon-14 labeled benzalacetophenone from a reaction mixture prepared from carbon-14-labeled benzaldehyde and nonradioactive benzalacetophenone has indicated the reversibility of this reaction through the dehydration step. Similarly, benzal-*o*-hydroxyacetophenone and dibenzalacetone have been shown to be formed by reversible processes. That the exchange process need not involve the reversible addition of water to the double bond has been demonstrated by the exchange of benzaldehyde- C^{14} with 2,4-dinitrostilbene in the presence of piperidine. Table 7 shows the results of such studies.

An interesting result of these base-catalyzed exchange studies has

Table 7

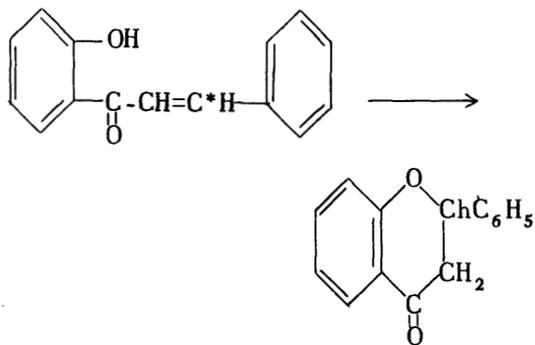
Results of Exchange Studies on Base-Catalyzed Condensation Reactions

REACTANTS	CATALYST	TEMPERATURE	TIME (hr)	EXCHANGE*	SOLVENT
$C_6H_5COCH=CHC_6H_5$ $C_6H_5C^{14}HO$	aq. NaOH	Room	12	+	ethanol-water
<i>o</i> - $HOC_6H_4COCH=CHC_6H_5$ $C_6H_5C^{14}HO$	aq. NaOH	Room	12	+	ethanol-water
$C_6H_5CH=CHCOOH$ $C_6H_5C^{14}HO$	aq. NaOH	Room	5.	-	ethanol-water
$C_6H_5CH=CHCOCH=CHC_6H_5$	aq. NaOH	Room	12	+	ethanol-water
$C_6H_5CH=CH-CH=CHCOC_6H_5$	aq. NaOH	Room	12	-	ethanol-water
3-benzalindene $C_6H_5C^{14}HO$	alc. KOH	65°C	4	+	methanol
$C_6H_5CH=CH-COOH$ $C^{14}H_3COOCO-CH_3$	CH_3COONa	170-5°C	4	-	none
2,4-(NO_2) $_2C_6H_3CH=CHC_6H_5$ $C_6H_5C^{14}HO$	piperidine	140°C	2	+	none
$C_6H_5COCH=CHC_6H_5$ $C_6H_5C^{14}HO$	none	100°C	48	-	none
$C_6H_5CH=CHCOOH$ $C_6H_5C^{14}HO$	piperidine	170°C	6	-	none
2,4-(HO) $_2C_6H_3CHO$ $C_2H_5OOC^{14}H$	KOC_2H_5	Room	24	-	ethanol

* + = exchange

- = no exchange

been the synthesis in high yield of carbon-14-labeled flavanone by ring-closure of the labeled benzal-*o*-hydroxyacetophenone prepared by exchange with carbon-14-labeled benzaldehyde.



Experimental

Friedel-Craft acylation reaction. The preparation of the labeled compounds has been described previously.⁽³¹⁾ In a typical experiment, 1 g of *o*-hydroxyacetophenone was added to 7.23 g of anhydrous aluminum chloride. Fifteen milliliters of anhydrous carbon disulfide was added with stirring. To this cooled mixture, 0.57 g of labeled acetyl chloride, dissolved in 15 ml of anhydrous carbon-disulfide was added. After eight days the ketone was isolated by adding ice and dilute hydrochloric acid and extracting with ether. The ether was distilled off and the semicarbazone of the ketone was prepared and purified by crystallization from ethanol. The semicarbazone, assayed by solid counting, was found to be nonradioactive.

An attempted exchange reaction between 2,4-dihydroxyacetophenone and acetyl chloride gave a product containing radioactivity. This product, though similar in many respects to 2,4-dihydroxyacetophenone, was proved

by infrared and ultraviolet absorption spectra to be different. Although it is apparently a condensation product of the ketone and the acetyl chloride, its identity has not been determined.

Base-catalyzed condensations. Benzaldehyde-7-¹⁴C was prepared as follows: Seven ml of benzyl alcohol, labeled in the 7 position and whose activity was approximately 2.52 $\mu\text{c}/\text{mmole}$, was suspended in 37.5 ml of water. To this mixture was added, with stirring, 5 g of chromium trioxide in 25 ml of water. The temperature was kept below 20°C. A solution of 4.5 ml of concentrated sulfuric acid in 25 ml of water was added to the cool solution. After vigorous stirring for 10 min. the mixture was extracted with chloroform. The chloroform solution, after washing with saturated sodium bicarbonate solution, was stirred with a saturated water solution of sodium bisulfite and cooled. The precipitated sodium bisulfite addition product was filtered off and air dried. This product was used in those experiments in which aqueous sodium hydroxide was the catalyst. In those reactions in which no water was used, anhydrous benzaldehyde was prepared from the bisulfite addition product by decomposing it with hot, saturated potassium carbonate solution, followed by steam distillation of the aldehyde. The benzaldehyde was separated from the distillate by ether extraction. The ether extract was dried and the ether removed by distillation.

In a typical experiment, 1 g of benzalacetophenone, 1.5 g of benzaldehyde sodium bisulfite addition product, 4 ml of ethanol, and 3 ml of water containing 0.2 g of sodium hydroxide were mixed and allowed to stand overnight with stirring. The

⁽³¹⁾ *Ibid.*

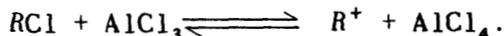
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mixture was acidified with hydrochloric acid and several volumes of water were added. The benzaldehyde was removed by steam distillation, and the yellow oil was extracted with ether. After the ether evaporated, the oil was crystallized several times from methanol and dried. Its identity was established as benzalacetophenone by comparison of its melting point and its mixed melting point with a sample of the authentic compound. The isolated compound was found to contain radioactivity.

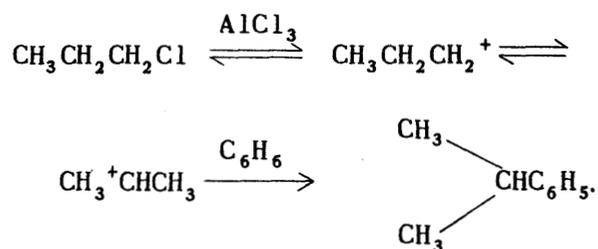
EFFECT OF ALUMINUM CHLORIDE ON ETHYLBENZENE

R. M. Roberts* G. A. Ropp
O. K. Neville

The alkylation of aromatic hydrocarbons with alkyl halides under the influence of aluminum chloride is considered to involve the intermediate formation of a carbonium ion:**



This carbonium ion, depending upon its freedom and stability, may attack the aromatic nucleus or it may rearrange prior to the attack. An example of such rearrangement is the condensation of *n*-propyl chloride with benzene to give isopropyl benzene:



*Member of the Research Participation Program sponsored jointly by the Oak Ridge Institute of Nuclear Studies and Oak Ridge National Laboratory; permanent address, University of Texas, Austin, Texas.

**In this discussion and that to follow the representation R^+ is an oversimplification. That the ion may never be free is possible, and that it might better be represented as an aluminum chloride solvent complex is recognized.

Friedel-Crafts alkylations are known to be reversible; thus alkyl groups may be reoriented on the aromatic nucleus or transferred intermolecularly under the influence of $AlCl_3$. The extent of isomerization within the chains during such migrations is not understood at present due to the lack of data and, in some cases, conflicting evidence.

Considerable evidence may be adduced from reactions involving carbonium ions as intermediates to show that the stability of these ionic intermediates is in the order tertiary > secondary > primary, and that such ions may rearrange to a more stable form by the shift of one or more hydride ions or methyl groups, e.g., isopropyl carbonium ion may be formed from the *n*-propyl species by the shift of one hydride ion.

Although the height of the interconversion energy barriers between two forms may be estimated from product analysis of certain reactions, the ease of conversion between two isomers of the same energy level can be determined only by labeling with isotopic carbon.

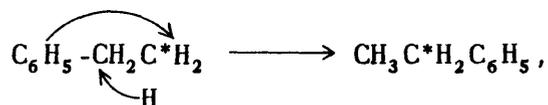
In the present case, the ease of isomerization of an ethyl carbonium ion to an isotopically isomeric ethyl carbonium ion has been studied by the



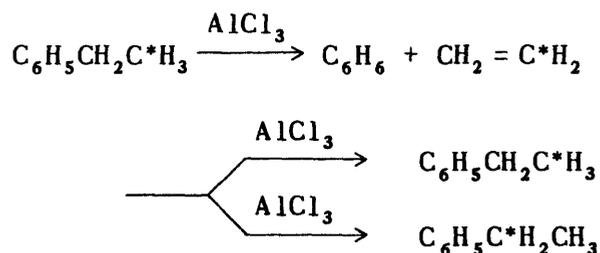
determination of the degree of migration of radioactivity from the beta to the alpha position of ethyl- β - C^{14} -benzene under various reaction conditions.

As a preliminary experiment ethylbenzene was treated with aluminum chloride under several reaction conditions. These experiments demonstrated that no isomerization was caused either in nitrobenzene solvent

or in the presence of solid catalyst. Isomerization was not promoted by the addition of α -chloroethylbenzene. These results indicated that intermolecular rearrangement of the type,



did not take place. Also, no symmetrical intermediate such as ethylene, or a complex of it, was involved, since recombination would result in random labeling.



These results could be explained by assuming either that no bond rupture occurred or that an unsymmetrical ethyl moiety was formed as an intermediate, which did not undergo rearrangement before recombination.

When ethylbenzene is heated at its boiling point with aluminum chloride, a fair yield of diethylbenzene may be isolated. This certainly involves intermolecular transfer of an ethyl group. When, however, ethyl- β - C^{14} benzene was converted in this manner to diethylbenzene no migration of radioactivity to the alpha position was observed. These results could be explained by assumption that the ethyl group moved from one aromatic nucleus to another without ever being free or that the intermediate formed did not rearrange. Again, no symmetrical intermediate was possible.

To distinguish between the two possibilities, ethyl chloride labeled in the beta position was condensed

with benzene in the presence of aluminum chloride. Under these conditions, there can be no doubt as to the free existence of some reactive ethyl intermediate. Again degradation revealed no migration of radioactive carbon.

These results could be explained either by assuming that the ethyl intermediate (carbonium ion) formed reacts faster with the aromatic nucleus than it isomerizes, or that the ethyl carbonium ion does not isomerize in the presence of aluminum chloride, i.e., the interconversion energy of primary-to-primary carbonium ion isomerization is too high.

To determine which explanation was better, ethyl chloride labeled in the beta position was allowed to stand over aluminum chloride at room temperature for 1 hr, which was the time required for condensation in the previous case. The ethyl chloride was recovered, purified by distillation, and condensed with benzene. Degradation revealed nearly complete isomerization, i.e., equal labeling in the two positions.

The best explanation of these novel results appears to be that the ethyl carbonium ion is transitory in existence and reacts with an aromatic nucleus before it can rearrange by migration of hydride ion. In the absence of an aromatic nucleus it can rearrange at a fair rate. The rate of this isomerization will be studied in an attempt to measure the activation energy of this primary-to-primary conversion.

TEST FOR REVERSIBILITY OF THE SULFURIC ACID DEHYDRATION OF FORMIC ACID

G. A. Ropp A. J. Weinberger

Because of an interest in the mechanism of the formic acid dehydration, a test was made to determine

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whether the rate of the reverse reaction (i.e., the absorption of carbon monoxide in the reaction mixture yielding formic acid) was appreciable. The test involved bubbling carbon-14 monoxide through a reacting mixture of sulfuric acid and unlabeled formic acid. When the period of bubbling-in of labeled gas was completed, and after the system was swept free of carbon monoxide, the dehydration was permitted to continue and a sample of carbon monoxide was collected. The low specific activity of this sample revealed that only a negligibly small per cent of the labeled carbon monoxide was absorbed in the reverse reaction.

Experimental. A reaction⁽³²⁾ evolving carbon monoxide was permitted to proceed at 0°C between 175 ml of cp sulfuric acid and 2.0 ml of formic acid azeotrope. During the first hour of reaction, 500 ml of carbon-14 monoxide (total activity 20 μc) was bubbled at a uniform rate through the reaction mixture. The system was then purged of all carbon monoxide by evacuation followed by sweeping with carbon dioxide for $\frac{1}{2}$ hr. As the reaction continued an ion chamber was filled (volume 250 ml) with the carbon monoxide produced. Radioassay revealed that the gas had an activity of only 4×10^{-3} μc per 500 ml.

DISPLACEMENT OF THE BENZOYL GROUP FROM PHENYL 9-FLUORENYL KETONE

J. G. Burr, Jr.

The action of formalin solution upon phenyl 9-fluorenyl ketone produces 9-methylenefluorene in strong alkaline solution and 9-benzoyl-9-fluorenyl carbinol in a weaker alkali solution. The existence of an equilibrium between 9-benzoyl-9-fluorenyl-

carbinol, phenyl 9-fluorenyl ketone, and formaldehyde has been established by tracer studies with carbon-14. 9-Benzoyl-9-fluorenylcarbinol gives 9-methylenefluorene in alkaline formaldehyde, and thus is the probable intermediate in the formation of 9-methylenefluorene from phenyl 9-fluorenyl ketone.

Experimental

Phenyl 9-fluorenyl ketone. The procedure of Werner⁽³³⁾ gave this product in 15% yield, which is in accord with the experience of others⁽³⁴⁾ using this method. Several attempts were made to prepare this compound in ether or benzene solution using sodium methoxide (which gave no product), and with sodium hydride (which gave an 18% yield). Finally, the use of potassium metal⁽³⁵⁾ gave a 64% yield of phenyl 9-fluorenyl ketone.

Reaction of phenyl 9-fluorenyl ketone (II) with alkaline formaldehyde solution. The ketone (0.5 g) dissolved rapidly in a mixture of 5 ml of ethanol and 5 ml of 50% aqueous potassium hydroxide. To the clear orange solution was added 5 ml of 37% formalin. After an induction period of about 1 min, the solution became turbid, and an additional 2 ml of formalin was added. In about 15 min the solution had become colorless and a granular white solid had precipitated. Ten ml of water was added and the solution stirred until all additional solid had coagulated. This solid, which weighed 0.32 g (97%) and melted at 40 to 50°C, was dissolved in hexane and filtered from

(33) A. Werner, "Über den wechselnden Affinitätswert einfacher Bindungen," *Ber.*, 39, 1287 (1906).

(34) W. Wislicenus and A. Fehrle, "Zur Darstellung den 9-Benzoyl-fluorens," *Ber.*, 48, 1320 (1915).

(35) *Ibid.*

(32) G. A. Ropp, A. J. Weinberger, and O. K. Neville, *loc. cit.*

the small amount of insoluble polymer. The filtrate absorbed bromine readily and deposited 0.40 g of massive pale yellow prisms, which melted at 141 to 142°C. Recrystallization from hexane did not change the melting point. A mixture of this with benzoylfluorene melted at less than 125°C.

Anal. Calcd. for $C_{14}H_{10}Br_2$: Br, 47.3. Found: 47.1.

When the aqueous filtrate from the formylation reaction was acidified and chilled, 0.16 g (71%) of benzoic acid crystallized whose melting point and mixture melting point with authentic benzoic acid (mp 119 to 120°C) was 119 to 120°C.

When the above reaction was carried out at steam-bath temperature, the precipitated product was an amorphous powder, which was very slightly soluble in benzene and hexane and insoluble in ether. It was infusible but showed shrinkage at about 300°C. These physical properties accord well with those of polymethylenefluorene. The same authors report 9-methylenefluorene as polymerizing with extreme readiness, even in the dark.

9-Benzoyl-9-fluorenylcarbinol. A solution of 0.50 g of phenyl 9-fluorenyl ketone in a mixture of 2 ml of ethanol and 2 ml of 50% aqueous potassium hydroxide was diluted with 5 ml of water and neutralized dropwise with 10% hydrochloric acid until faint permanent cloudiness resulted. The resulting solution was treated with 10 ml of water followed by 10 ml of 37% formalin. A yellowish gum precipitated almost immediately. Ether extraction of the gum separated about 0.1 g of polymethylenefluorene. The ether-soluble substance (0.45 g) deposited from hexane 0.20 g of colorless prisms, which melted at 121 to

124°C. Recrystallization from hexane gave 0.18 g of prisms melting at 123 to 124°C. Mixture melting points of this substance with benzoylfluorene (mp 135 to 136°C) and with fluorene-methanol (mp 99 to 100°C) showed marked depressions.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.36. Found: C, 84.0, 84.3; H, 5.51, 5.61.

To determine the reaction with alkali, another portion of the substance (0.45 g) was stirred for 1 hr with a mixture of 15 ml of ethanol and 10 ml of 50% aqueous potassium hydroxide (the solution was homogenous and orange in color), then diluted with 100 ml of water. A small amount of oily orange precipitate was filtered off and the filtrate acidified. The pale yellow precipitate (0.30 g) was crystallized twice from hexane to give 0.15 g of benzoylfluorene whose melting point and mixture melting point with authentic benzoylfluorene (mp 135 to 136°C) was 135 to 136°C.

To determine the cleavage, a similar amount of the material (0.45 g) was suspended in a mixture of 5 ml of ethanol and 5 ml of 37% formalin. To this solution was added 5 ml of 50% aqueous potassium hydroxide, and then 2 ml of formalin. A deep orange color developed immediately and swiftly faded. The flocculent precipitate which formed, when worked up as above, gave 0.50 g of 9-brom-9-bromomethyfluorene (mp 141 to 142°C).

Reaction of 9-benzoyl-9-fluorenylcarbinol with alkaline formaldehyde- C^{14} solution. A suspension of 0.50 g (1.67 mmoles) of the benzoylfluorene methanol III in a mixture of 5 ml of ethanol and 7 ml of 10% formaldehyde- C^{14} (containing 23 mmoles of $C^{14}H_2O$ with a specific activity, as determined on the dimedon derivative, of 4.24 μ c of C^{14} /mmole) was stirred with 5 ml

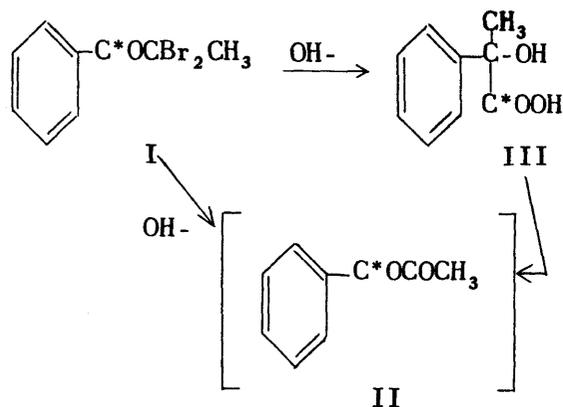
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of 50% aqueous potassium hydroxide for ½ hr. The fluffy solid that precipitated (0.25 g) was filtered, dissolved in hexane, refiltered, and the solution was treated with bromine. On chilling, 0.15 g of dibromide crystallized. After recrystallization from hexane, this was found to contain 4.01 μc of C^{14} /mmole (calculated for complete equilibrium, 3.96 μc of C^{14} /mmole). The aqueous filtrate was mixed with a saturated aqueous dimedon solution. The precipitated formaldehyde derivative was found to contain 3.99 μc of C^{14} /mmole.

REARRANGEMENTS OF α -DIKETONES

E. C. Hendley* O. K. Neville

α,α -Dibromopropiophenone I, labeled with carbon-14 in the carbonyl group, has been shown previously⁽³⁶⁾ to give atrolactic acid III labeled exclusively in the carboxyl group, thus demonstrating 100% phenyl-group migration in the alkaline catalyzed rearrangement.



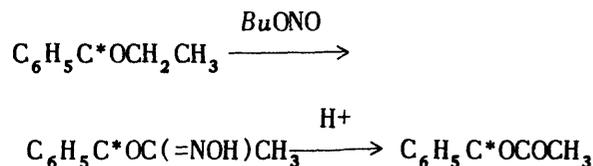
*Member of the Research Participation Program sponsored jointly by the Oak Ridge Institute of Nuclear Studies and Oak Ridge National Laboratory; permanent address, Mississippi State College, State College, Mississippi.

⁽³⁶⁾K. S. Warren and O. K. Neville, "Rearrangement of α,α -Dibromopropiophenone," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951*, ORNL-1116.

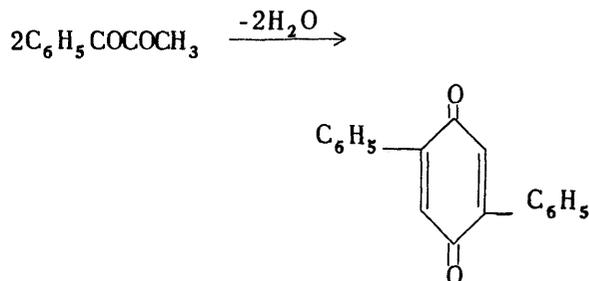
The reaction is postulated⁽³⁷⁾ to involve the intermediate formation of methyl phenyl diketone II, which then undergoes a benzilic acid type of rearrangement.

Since such a reaction path is not the only plausible scheme that can be written, it has been of interest to study the base-catalyzed rearrangement of methyl phenyl diketone itself.

Methyl phenyl diketone, labeled in the carbonyl group adjacent to the benzene ring, was prepared by the treatment of carbonyl-labeled propiophenone with butyl nitrite followed by acid hydrolysis of the resultant monoxime.



When methyl phenyl diketone was subjected to the same conditions of rearrangement as those used with the dibromide I, no atrolactic acid was recovered. The sole product was 2,5-diphenylbenzoquinone, formed by aldol condensation between two molecules of diketone.



In order to avoid this competing condensation it was necessary to

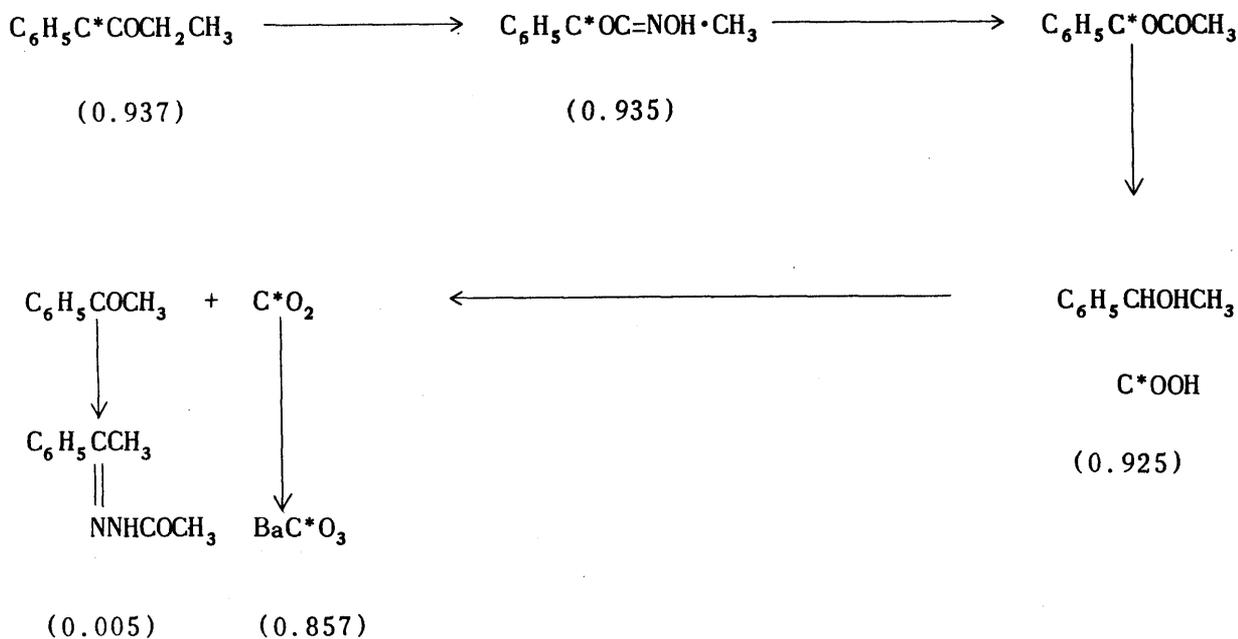
⁽³⁷⁾R. Levine and J. R. Stevens, "Course of the Oxidation of Propiophenone with Alkaline Hypobromite Solution and Certain Related Reactions," *J. Am. Chem. Soc.*, 72, 1642-4 (1950).

carry out the reaction at high dilution, so that the possibility of reaction between two organic molecules was reduced. Since methyl phenyl diketone is very slightly soluble in water, a convenient method involved the use of a two-phase system. The diketone, dissolved in a large volume of ether, was stirred vigorously for 1 hr with an equal volume of 20% sodium hydroxide solution maintained at 0°C. Under these conditions a yield of about 25% of the desired atrolactic could be isolated after neutralization of the aqueous layer.

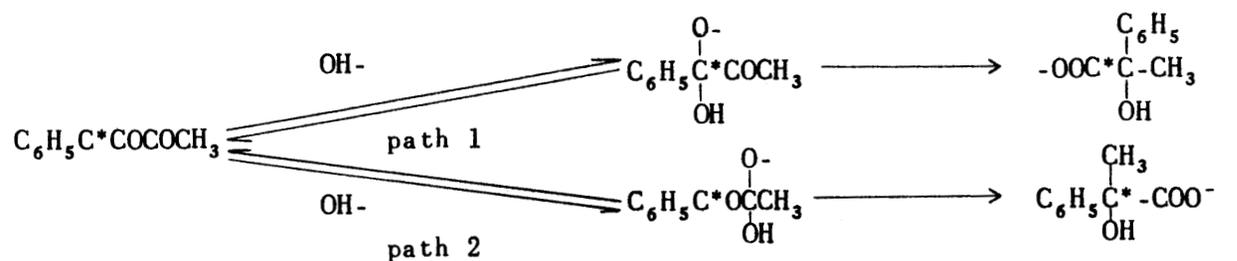
The atrolactic acid was degraded by oxidation to acetophenone and carbon dioxide. Since no radioactivity was found in the acetophenone, the rearrangement must have occurred with 100% phenyl-group migration. In the scheme below, the radioactivities in microcuries per millimole are shown by the appropriate structures of the compounds studied.

These results indicate that a reaction path involving the intermediate formation of the methyl phenyl diketone cannot be excluded in the rearrangement of α, α -dibromopropiophenone. If this is the mode of reaction it is obvious that the rate of rearrangement of the diketone must be much faster than the rate of its formation, i.e., its concentration at any time must be so low as to preclude condensation between two molecules.

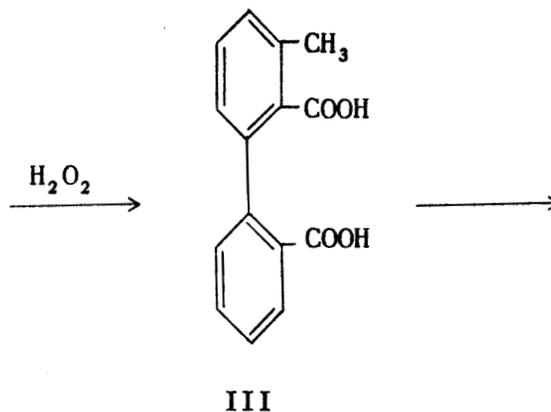
If the rearrangement of methyl phenyl diketone to atrolactic acid is considered to be of the benzilic acid type, the reaction would involve the rapid reversible addition of hydroxyl ion to one carbonyl group, followed by migration of the adjacent group. The reaction path followed would then be a function of the relative reactivities of the two carbonyl groups toward hydroxyl ion attack, and of the relative ease of migration of the phenyl and methyl groups.



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From the results given above it is obvious that path 2 is eliminated. In most of the previously studied cases the first, or hydroxylation step, has appeared to be the controlling one in determining which reaction path was followed. In the present case the second, or rearrangement step, is apparently more important, since it is difficult to justify the experimental results by the assumption of a tremendous difference in carbonyl group affinities for hydroxyl-ion attack.

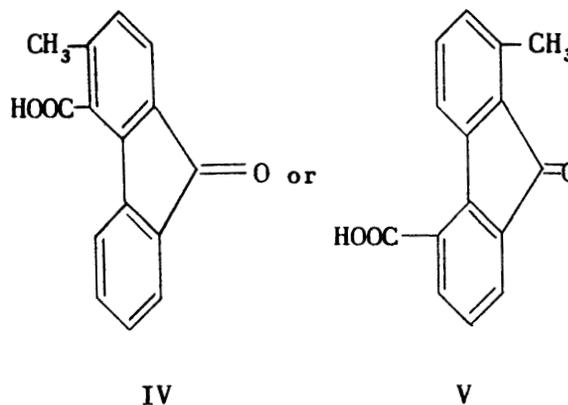
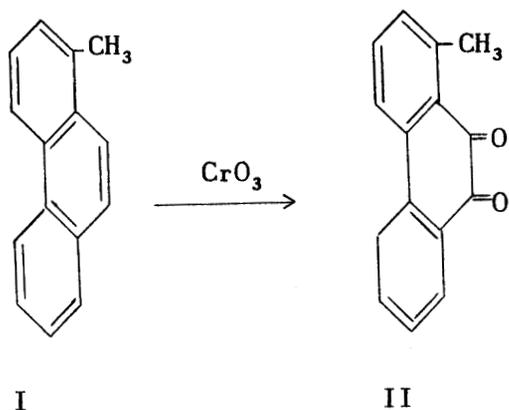


STRUCTURE DETERMINATION STUDIES

1-METHYLPHENANTHRENE-9(10)-C¹⁴

B. M. Benjamin* C. J. Collins

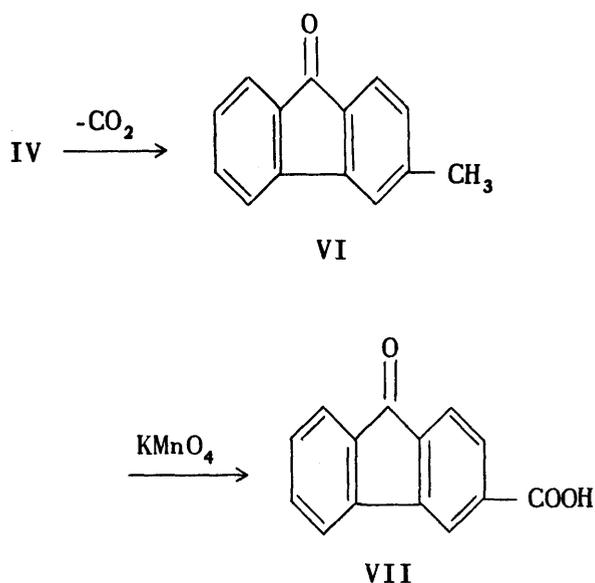
1-Methylphenanthrene I has been degraded to a single methylfluorene-carboxylic acid IV or V by methods



described in a previous report.⁽³⁸⁾ This acid, which is obtained in a yield of 75% by ring closure of the dicarboxylic acid III, has been shown to possess structure IV by decarboxylation and oxidation to the known keto-acid VII.

*Oak Ridge Institute of Nuclear Studies Graduate Fellow from the University of Florida, Gainesville, Florida.

(38) B. M. Benjamin and C. J. Collins, "Synthesis and Structure Determination of Carbon-14 labeled 1-Methylphenanthrene," *Chemistry Division Progress Report for Period Ending March 31, 1951*, ORNL-1053, p. 75.



Experimental. A sample of methyl-fluorenonecarboxylic acid weighing 82.6 mg was placed in a flask with 5 g of dibenzyl amine, 5 g of tribenzyl amine, and 100 mg of copper chromite. The temperature was raised rapidly until reflux began, whereupon gas was emitted almost all at once and precipitate was formed in a $\text{Ba}(\text{OH})_2$ trap. Heating was continued while passing helium through the reaction mixture, but no more precipitate formed in a fresh $\text{Ba}(\text{OH})_2$ trap. After cooling, an excess of 6 N HCl was added to the reaction mixture, and the mixture was extracted with ether. Removal of ether in an air stream left an oily brown residue which was inert toward bicarbonate and would not crystallize upon cooling. When the residue was taken up in hot 80% ethanol and the solution was cooled, the oily residue again separated. Rapid cooling again did not cause crystallization. All solvents were removed. To the oily residue was added 50 ml of a 2% solution of KMnO_4 ,

and the mixture was heated with refluxing for 3 hr. A little bicarbonate was added and the solution was extracted with ether. Acidification of the aqueous layer followed by ether extraction gave a yellow acid melting at 280°C without further purification. Fluorenone-3-carboxylic acid is reported⁽³⁹⁾ to melt at 285 to 286°C , while the other possible isomer, fluorenone-1-carboxylic acid⁽⁴⁰⁾ melts at 191 to 192°C .

CHRYSENE-5,6- C_1^{14}

D. N. Hess C. J. Collins

The procedure for the degradation of chrysene-5,6- C_1^{14} I⁽⁴¹⁾ has now been accomplished, using unlabeled chrysene for the model experiments. Since the scheme has not yet been applied to the chrysene-5,6- C_1^{14} I, the experimental procedure will be given in a later report.

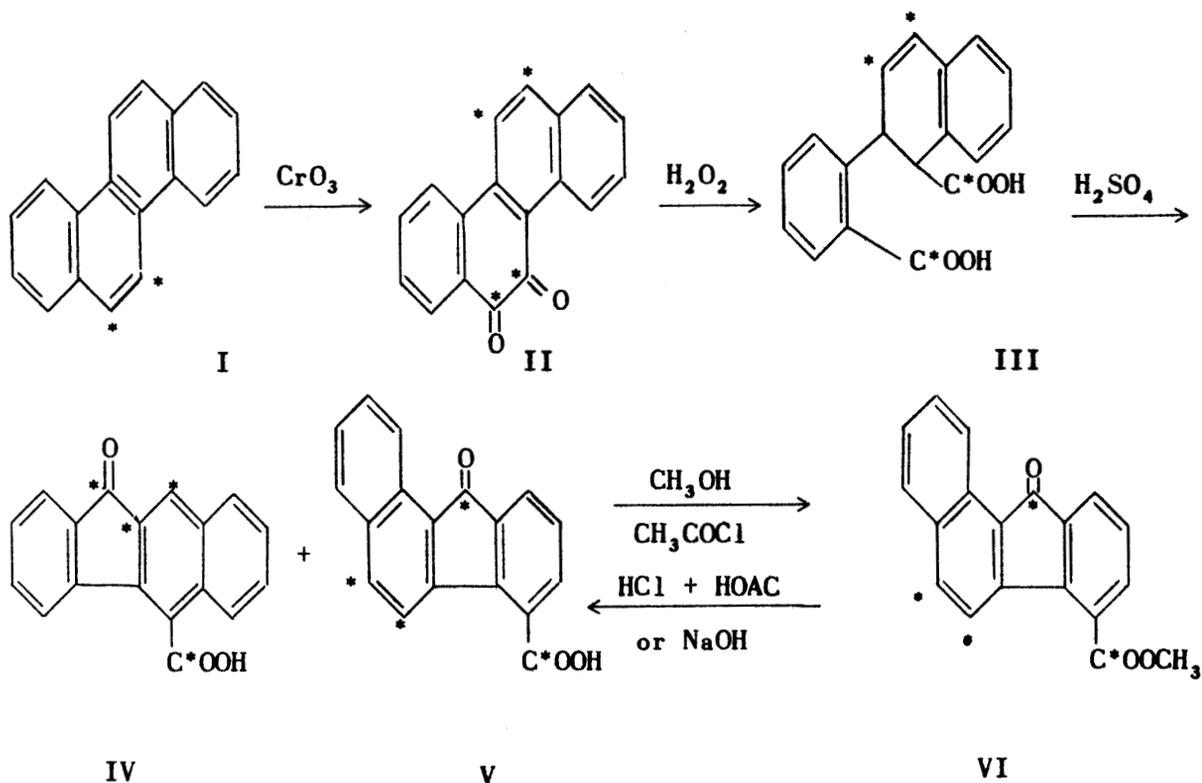
Ring closure of the acid III has now been found to yield a mixture of two keto acids, IV and V. (The asterisks are included in the formulas to show how the scheme will apply to the labeled chrysene.) When this mixture is boiled with methanol containing a catalytic amount of acetyl chloride, only one methyl ester VI is formed. The acid IV can then be

(39) O. Kruber, "Beitrag zur Kenntnis der höhersiedenden Fraktionen des Steinkohlenteer-Schweröls," *Ber.*, 65B, 1382-6 (1932); A. Sieglitz and J. Schatzkes, "Über ein Synthese der Isodiphensäure," *ibid.*, 54, 2070-1 (1921).

(40) R. Fittig and H. Liepmann, "Fluoranthren," *Ann.*, 200, 6 (1879).

(41) C. J. Collins, A. R. Jones, and G. M. Toffel, "The Mechanism of the Wagner Rearrangement. II. The Synthesis of Chrysene-5,6- C_1^{14} ," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, ORNL-795, p. 78.

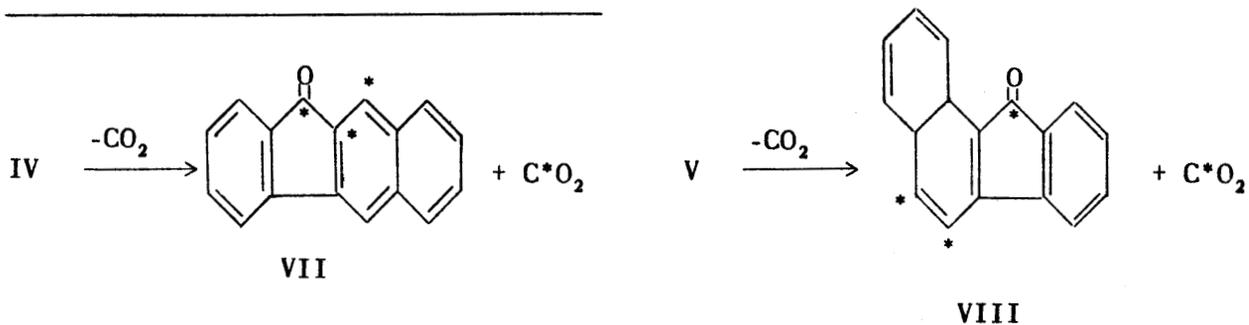
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removed quantitatively by the action of sodium bicarbonate solution.

Both keto acids have been decarboxylated to yield ketones VII and VIII. Inspection of the reaction sequence shows that an assay of the

labeled ketone VII should be a measure of the carbon-14 in the 6 position of the chrysene I, whereas an assay of the labeled ketone VIII should be a measure of the carbon-14 in the 5 position of the chrysene I. A tracer run is now in progress.



CHEMISTRY OF SEPARATIONS PROCESSES

FLUORIDE STUDIES

P. A. Agron

REMOVAL OF PROTACTINIUM-233 FROM NEUTRON IRRADIATED ThF₄

In the fluoride volatilization of protactinium from irradiated ThF₄ it was observed that relatively large fractions were removed in the initial runs where a platinum boat had been used.⁽¹⁾ In these experiments the platinum had been largely converted to PtF₄ and volatilized away from the

sample. A series of experiments using freshly prepared PtF₄ were performed in a standard manner to eliminate the effect of the heat generated in the conversion of the platinum to its fluorides. A comparison of the effectiveness of PtF₄ plus fluorine vs. comparable fluorine and PF₃(g) treatments in the removal of protactinium is illustrated in Table 8.

With a background of experimental data at Brookhaven, a pelleted sample of ThF₄⁽²⁾ was used here for the extraction studies. Several chips

Table 8

Extraction of Protactinium-233 from ThF₄

RUN*	ThF ₄ SAMPLE	TREATMENT	TEMPERATURE (°C)	TIME (hr)	FRACTION OF ACTIVITY REMOVED
C-1	27K	F ₂ , 1 atm	600	4.5	0.0036
C-2		F ₂ , 1 atm	600	4.5	0.0032
D-0	98K	PF ₃ (g) (300 psia)	375-400	5	
D-1		F ₂ , 1 atm	600	4	0.0045
D-2		F ₂ , 1 atm	600	4	0.0029
E-0	98K	Pt + F ₂	500 550	1 0.25	
E-1		0.4 g PtF ₄ + F ₂	600	4	0.20
E-2**		PtF ₄ + F ₂	600	3.5	0.06
F-1	90K	0.38 g PtF ₄ + F ₂	600	4	0.12
F-2		0.30 g PtF ₄ + F ₂	600	2	0.01
F-3		0.34 g PtF ₄ + F ₂	600	3.5	0.0065
G-1	27K	0.47 g PtF ₄ + F ₂	500	6	~0.012***
G-2		0.24 g PtF ₄ + F ₂	500	4	0.007

*Each letter indicates a different series of treatments; each number indicates consecutive extractions.

**Small residue of PtF₄ from previous run in nickel boat.

***Spill on removal of foil, therefore, only one-half of foil used and total activity estimated.

⁽¹⁾P. A. Agron and E. G. Bohlmann, "Volatility," Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951, ORNL-1116.

⁽²⁾Surface Area, $6 = 0.48 \text{ m}^2/\text{g}$. Designated by Brookhaven National Laboratory as Sample N - 233 - 13 - 1.

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of the above material were exposed in the X-10 graphite reactor for 16 hr at a flux of 5×10^{11} neutrons/cm²/sec. The sample was then divided into three portions of 0.12 g each and treated as indicated in an all-nickel system.

Table 8 lists the conditions used and the fractions of protactinium removed from the irradiated ThF₄.

The data in Table 8 indicate that the presence of PtF₄ markedly facilitates the removal of protactinium from ThF₄ at 600°C. The mechanism whereby this is effected is not known. However, it was observed in several of the experiments that when PtF₄ was not completely volatilized the chips of ThF₄ were yellow in appearance, indicating perhaps adsorption of PtF₄ on the ThF₄ or compound formation. Runs G-1 and G-2 indicate that the rate of removal in the presence of PtF₄ at 500°C is higher than that using fluorine alone at 600°C. Runs E-1 and F-1 indicate a mean hold-up time of less than 10 days. These results suggest that it may be advisable to investigate the use of other volatile fluorides with lower neutron capture cross sections, such as BiF₅.

PROTIUM-DEUTERIUM EXCHANGE

P. A. Agron J. Halperin

It may be desirable to process a homogeneous reactor D₂O solution directly with protonated ion-exchange resins or organic solvents in which only the readily replaceable hydrogen atoms are deuterated. One of the factors determining the feasibility of such a procedure is the exchange of the deuterium in the D₂O with the ordinary hydrogen in the organic phase under radiation. A study has been started for the purpose of measuring such exchange. Preliminary work has been performed in setting

up a gradient tube and the necessary thermostating bath with which to measure water density and thus deuterium content.

ORGANIC CHEMISTRY OF SOLVENTS

W. H. Baldwin C. E. Higgins

THE RATE OF HYDROLYSIS OF TRI-N-BUTYL PHOSPHATE

Studies on the rate of hydrolysis of tri-n-butyl phosphate have been delayed while analytical methods are being developed. The products of this hydrolysis are being prepared in pure form both with and without labeled phosphorous. These are to be used as carriers and tracers in the analytical work.

EXTRACTION OF ZIRCONIUM AND URANYL IONS INTO ORGANIC SOLVENTS USING DIBENZOYLMETHANE

J. P. McBride

The desirability of having a chelating agent with a low solubility in water prompted an investigation of the applicability of dibenzoylmethane (DBM) in a solvent extraction system. It has been found to be very much less effective than TTA (thenoyl-trifluoroacetone) as an extracting agent for Zr⁺⁴ and UO₂⁺².

Benzene solutions of DBM made by Eastman Kodak were equilibrated (40 hr shaking) with 3M HClO₄ solutions containing zirconium-95 tracer. Only negligible extraction was observed. Aliquots of a stock TTA-benzene solution were added to each benzene phase and the mixtures reagitated in order to test the extractability of the tracer. The distribution ratios observed in the systems containing both DBM and TTA were greater than predicted by a simple addition of the expected extraction from each chelating agent acting independently. The formation of a mixed chelate is a

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likely explanation of this phenomenon. It would be of interest to investigate the effect of the addition of DBM on the efficiency of cation separations by the TTA extraction method.

Table 9 summarizes the data obtained. An apparent slight extraction is observed in the absence of both DBM and TTA. Since the HClO_4 tracer solution was prepared by stripping the zirconium-95 from a TTA-benzene solution and washing the resulting aqueous phase with fresh benzene, the extraction may be due to a small amount of TTA remaining in the aqueous phase. The DBM distribution ratios were calculated from organic aliquots having from 9 to 100 gamma c/min and, hence, are subject to considerable error. They indicate, however, an equilibrium constant for the extraction of zirconium of the order of 10^3 , compared to the order of about 10^9 for TTA.

One experiment was run to test the efficiency of extraction of uranium-233 tracer from 0.02 M HCl with 0.5 M DBM benzene. An extraction constant

of about 10^{-4} was observed, compared with about 10^{-2} for TTA.

A new scintillation counter containing a sodium iodide crystal has been installed in the laboratory. The crystal, which is 2 in. thick and $1\frac{1}{2}$ in. in diameter, has a hole drilled along the axis of the cylinder $1\frac{1}{2}$ in. deep which accommodates a small test tube. The material to be counted is placed in the tube and inserted in a metal receptacle contained in the crystal hole. The counting rate was then followed as a function of volume by diluting with aqueous acid. Figure 8 illustrates the data obtained.

Larger variations as a function of volume were noted for the lower energy gamma. In both cases, however, the maximum in the count rate appears between 0.5 and 0.8 ml. (Actually the height of the sample in the tube is a more important variable than volume, and samples for counting should be diluted to the same height rather than to equal volumes before counting.)

Table 9

Extraction of Zirconium-95 from 3 M HClO_4 with Dibenzoylmethane

INITIAL DBM CONCENTRATION	$D \frac{o}{a}$	CONCENTRATIONS AFTER TTA ADDITION		$D \frac{o}{a}$	PREDICTED** $D \frac{o}{a}$	FACTOR OF INCREASE in $D \frac{o}{a}$
		DBM	TTA			
0	0.003	0	0.016	0.96	(0.96)	-
0.025	0.002	0.016	0.010	0.32	0.15	2.1
0.050	0.005	0.033	0.012	0.79	0.30	2.6
0.075	0.005	0.049	0.014	1.54	0.56	2.8
0.100	0.009	0.065	0.016	3.63	0.96	3.8
0.125	0.013	0.081	0.020	10.8	2.35	4.6
0.150	0.023	0.098	0.024	15.3	4.9	3.1

* D = distribution ratios

** Calculated from the observed $D \frac{o}{a}$ at 0.016 M TTA assuming a fourth-power TTA dependence.

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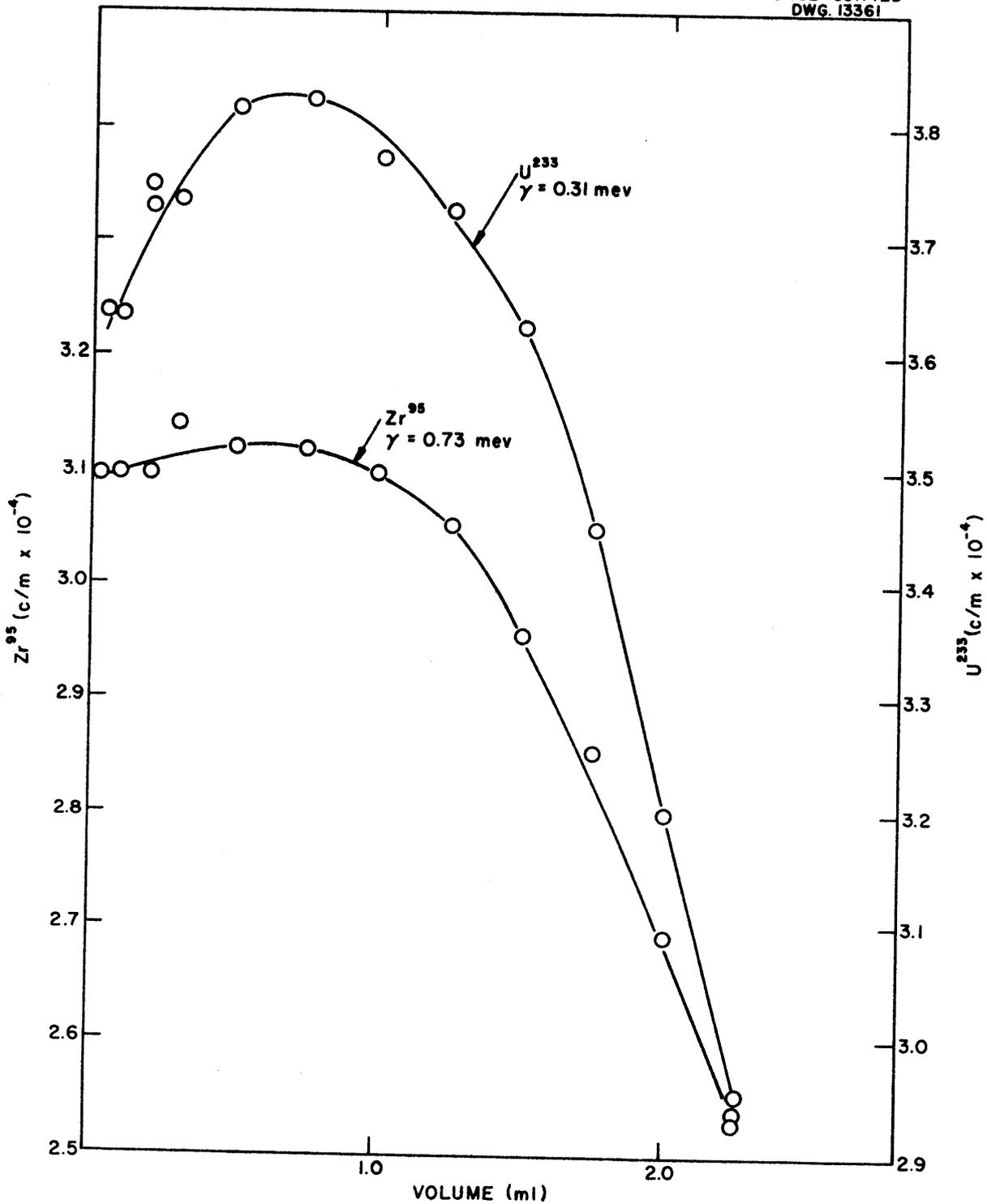


Fig. 8. Effect of Sample Volume on Gamma Counting Rate of Scintillation Counter.

To test the linearity of response of the counter, aliquots of a zirconium-95 tracer were counted. All counting samples were diluted to the same height before counting. Essentially no deviation from linearity was observed up to 140,000 c/min.

The gamma count for uranium-233 tracer as measured on this counter at a sample volume of 750 μ l is 1.2×10^{-3} per alpha disintegration.

ADSORPTION OF THENOYLTRIFLUOROACETONE AND ITS URANYL CHELATE FROM ORGANIC SOLVENTS

The use of thenoyltrifluoroacetone (TTA) for the extraction of large quantities of uranium entails the use of a high concentration of TTA over and above the stoichiometric amount required for the formation of the chelate. The excess TTA makes subsequent stripping of the cation back into an aqueous solution difficult because of the very large dilution required to reduce the TTA concentration to a usable value. In view of this it was considered desirable to investigate the possibility of a chromatographic separation of the excess TTA from its uranyl chelate. If such a procedure were to prove feasible, it would be employed before or during the stripping operation. The following is a report on the preliminary batch adsorption experiments performed on this problem. Since for various reasons no further work is planned for the immediate future, it was felt proper to report the work in detail at this time although no conclusion as to the feasibility of such a separation has been reached.

MATERIALS OF RESEARCH

The activated alumina used was Fisher adsorption alumina; the bone charcoal, Baker and Adamson granular material; the titania, Baker and

Adamson anhydrous cp reagent; and the alundum, Norton Co. refractory grain RR Alundum. The silica gel was Merck reagent-grade silicic acid, which was boiled with concentrated HCl, washed with water and alcohol, dried at 110°C, and sieved to 100 to 200 mesh. The zirconia was A. D. Mackay cp zirconium hydroxide, which was refluxed with alcohol and dried overnight at 200°C.

The thenoyltrifluoroacetone was obtained from the University of California Radiation Laboratory, vacuum distilled twice, and dried over P_2O_5 before use. The melting point of the purified product was 140 to 141°C.

The uranyl TTA chelate was prepared by mixing a UO_2SO_4 solution with the stoichiometric amount of TTA in benzene, partially neutralizing with NH_4OH the acid liberated in the extraction, and pulling off the benzene by suction. The resulting red-orange precipitate was washed thoroughly with water and benzene—the latter to remove excess TTA. After air drying, the chelate was allowed to stand over $CaCl_2$ in an evacuated dessicator.

EXPERIMENTAL

Adsorption of TTA. The TTA adsorption experiments were performed by mixing 2 ml of a 0.05 M TTA solution in the solvent to be tested with $\frac{1}{2}$ g of an adsorbent and equilibrating overnight. The TTA concentration before and after contact with the adsorbent was determined by diluting by a factor of 10^3 with benzene (irrespective of the solvent) and measuring the optical density on a spectrophotometer. Adsorbents, other than charcoal, produced less than 10% decrease in the total volumes of the solutions whereas charcoal absorbed about 25% of each solvent tested. Preferential adsorption of the TTA

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Table 10

Adsorption of TTA from Organic Solvents

Conditions: 2 ml 0.05 M TTA

0.5 g adsorbent

SOLVENT	PER CENT DECREASE IN TTA CONCENTRATION					
	ALUMINA	BONE CHARCOAL	SILICA GEL	ZIRCONIA	TITANIA	ALUNDUM
Benzene	98	92	12**	23	8	0
Carbon tetrachloride	98	90	63	29	6	0
Dibutyl carbitol	*	25	6	10	0	9
Hexone	-	-	21	-	-	10

* Changes occurring in optical spectra upon contact with alumina make data difficult to interpret, as explained in the section of this report on "Adsorption of TTA and Uranyl TTA Chelate from Dibutyl Carbitol."

** 0.135 M TTA-benzene was used.

is shown by the data in Table 10, which records the per cent decrease in TTA concentration in the solvents.

Adsorption of Uranyl TTA Chelate. Sufficient uranyl TTA chelate to give 0.025 M solutions was added to each of the four solvents mentioned above, which were dried before use by agitation with activated alumina. Benzene and carbon tetrachloride failed to dissolve the chelate completely after intermittent shaking for several hours. Approximate chelate solubilities of 0.006 M for benzene and 0.0004 M for carbon tetrachloride were indicated. A slight yellow precipitation was observed in the dibutyl carbitol and hexone solutions of the chelate. This was centrifuged out before use and additional precipitation seemed not to occur on standing.

To eliminate the possibility that the precipitation observed above was an impurity in the chelate, additional chelate was recrystallized from

benzene and dissolved in hexone. Slight precipitation was again observed. Since water was found not to decompose the chelate rapidly, the precipitation is probably the result of some decomposition reaction occurring in or with the hexone or some impurity therein.

Two-ml aliquots of the chelate solutions were equilibrated overnight with ½-g quantities of activated alumina. Essentially complete adsorption of the chelate was obtained from benzene, carbon tetrachloride, and hexone as indicated by the complete removal of the yellow color from the solutions. Concentrations of the chelate less than 2.5×10^{-5} M give an easily perceptible yellow color. Incomplete adsorption was obtained from the dibutyl carbitol solution, but changes in the optical adsorption spectra of the chelate brought about by contact with the alumina made interpretation difficult. These will be discussed

below. In other adsorption experiments, using the chelate-hexone solutions and silica gel and alundum as adsorbents, no preferential adsorption of the chelate on the adsorbents was observed.

Adsorption of TTA and Uranyl TTA Chelate from Dibutyl Carbitol. The adsorption experiments using TTA-carbitol and chelate-carbitol solutions and activated alumina gave very different results from those obtained with the other solutions. Figures 9 and 10 show the optical adsorption spectra obtained using the TTA and chelate solutions before and after contact with the alumina. The broken line in Fig. 10 is the spectrum obtained using the chelate-hexone solution. (Of course, all spectra were obtained after the solutions were diluted with benzene, as mentioned previously.) The spectra obtained after contact resemble very closely the aluminum TTA chelate spectrum in benzene.⁽³⁾ Presumably, in the TTA case, the TTA reacts with the adsorbent to form the aluminum chelate, which is not adsorbed. In the uranyl chelate case, partial decomposition of the chelate occurs before and/or during the adsorption process. It may be that the aluminum chelate was also formed during the adsorption experiments involving the other solvents and alumina, and that the aluminum chelate would have been the substance eluted by the addition of an eluting agent to these systems.

RATE STUDIES WITH ION EXCHANGERS

B. A. Soldano G. E. Boyd

During the past quarter several new and interesting findings have

⁽³⁾E. L. Zebroski, *Chelate Chemistry of Thenoyltrifluoroacetone and Acetylacetone and Hydrolysis Phenomena of Thenoyltrifluoroacetone*, EC-63, July 1, 1947, Part III, p. 16.

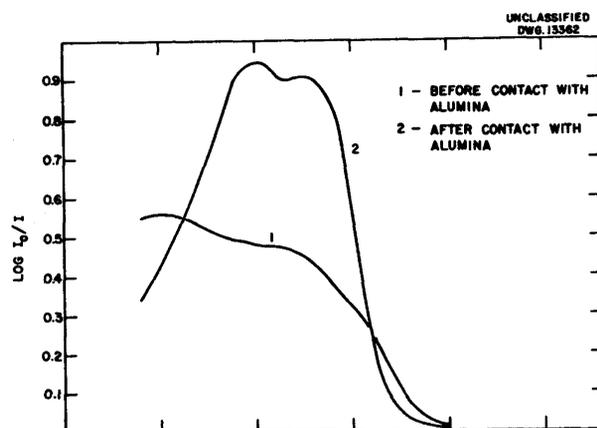


Fig. 9. Spectral Changes Produced in TTA - Dibutyl Carbitol by Alumina.

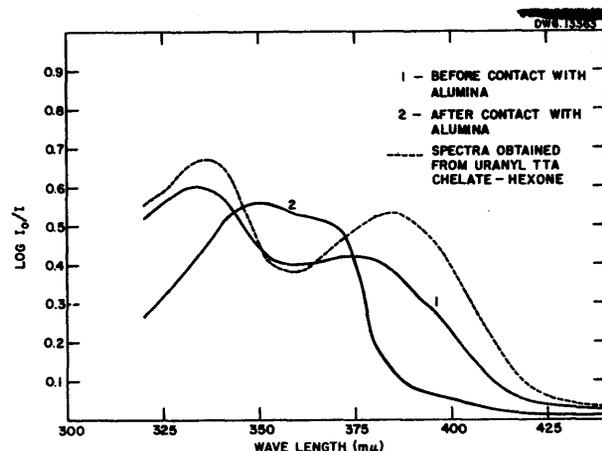


Fig. 10. Spectral Changes Produced in Uranyl TTA Chelate-Dibutyl Carbitol by Alumina.

been made in studies on the self-diffusion of ions in various ion-exchange materials. Three types of preparations were examined: (1) Dowex-50 type sulfonic acid cation exchangers of varying capacity produced by desulfonation; (2) Dowex-1 type anion exchangers in which the nature of the exchange group was systematically varied; (3) a chelating resin shown to exhibit a high specificity for transition group elements. Although a detailed account of the first two researches cannot be given here,

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Table 11

Self-diffusion of Cations in a Chelating Resin

ION	$D_{25^{\circ}}$ ($\text{cm}^2 \text{sec}^{-1}$)	$D_{0.3^{\circ}}$ ($\text{cm}^2 \text{sec}^{-1}$)	$E_{\text{act.}}$ (cal/mole^{-1})
K^+	9.12×10^{-7}	2.93×10^{-10}	17,500
Ag^+	4.27×10^{-9}		
Co^{++}	5.05×10^{-9}		
Zn^{++}	1.09×10^{-9}		

several results may be noted: Both equilibrium selectivity⁽⁴⁾ and rate measurements were conducted on the desulfonated cation exchangers in order to determine the effect of variable capacity at constant cross-linking. Surprisingly, with the sodium-hydrogen and silver-sodium equilibria, large increases in selectivity for the H^+ and Ag^+ ions, respectively, were found. These increases are in the direction of favoring those ions tending to form poorly dissociated ion pairs. In the past, the ions in an ion exchanger have been regarded as dissolved in the water of gelation. These new results, however, strongly indicate that the over-all dielectric constant of the exchanger phase is of decisive importance, and that the ions in an exchanger may be more properly regarded as dissolved in a mixed aqueous-organic solvent. The rate of ionic self-exchange in the desulfonated preparations decreased with decreased capacity and the activation energy increased. With very low-capacity exchangers the activation energy exceeded 10 kcal/mole.

Measurements of the self-diffusion of anions in eleven different quater-

nary ammonium-type anion exchangers showed that the structure and composition of the exchange group may be of prime importance. A linear relation between the logarithm of the self-diffusion coefficient of bromide ion and its activation energy for diffusion was obtained with exchangers derived from homologous series of tertiary amines. In general, the rate decreased as either the size or the polarity of the exchange group increased.

Some time ago preliminary experiments were performed using a cationic chelating resin (XE-102) made available to us through R. Kunin of the Rohm and Haas Company. Comparisons were made between the rates of self-exchange of strontium and cupric ions, respectively, using appropriate radioactive tracers. The former ion reacted rapidly and reversibly, whereas the latter showed no self-exchange even after many hours. Further measurements (Table 11) on the self-diffusion of potassium, silver, cobalt, and zinc ions have revealed that in some cases at least the reaction velocities are such that quantitative rate constants can be obtained.

Potassium ion was found to self-diffuse quite rapidly and at a rate which may be compared with that observed for a nominal 5.5% DVB Dowex-50 type exchanger. Silver, cobaltous,

⁽⁴⁾Performed by O. D. Bonner, Department of Chemistry, University of South Carolina, Summer Research Participant.

FOR PERIOD ENDING SEPTEMBER 30, 1951

and zinc ions, however, diffused in the chelating resin far more slowly than in Dowex-50 (D_{25}^c for Zn^{++} in 5% DVB Dowex-50 $\approx 1.9 \times 10^{-7}$). Further, cationic charge was of little im-

portance, and quite large activation energies were observed. As expected, this chelating resin is specific for the cations of the transition group elements.

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CHEMICAL PHYSICS

NEUTRON DIFFRACTION STUDIES

H. A. Levy S. W. Peterson

THE CRYSTAL STRUCTURE OF POTASSIUM BIFLUORIDE

The question of the nature of the hydrogen bond in the bifluoride ion has attracted much experimental and theoretical treatment. X-ray crystallography has shown that the two fluorine atoms in potassium bifluoride are separated by the short interatomic distance of 2.26 Å. The location of the proton, which is presumed responsible for the binding, has been the aim of several investigations. If the forces in the bifluoride ion are chiefly electrostatic the proton would be expected to be centrally located between the fluorine atoms. If exchange forces are important a potential function with a double minimum might be expected and the proton would be located at random in two positions close to either fluorine atom. Ketelaar,⁽¹⁾ and also Glockler and Evans,⁽²⁾ utilizing infrared data, came to the conclusion that the double minimum model was the correct one. Their respective calculations⁽³⁾ led to distances of 0.70 and 0.52 Å between the potential minima. Some doubt was cast upon these conclusions by the dielectric constant measurements of Polder⁽⁴⁾

(1) J. A. A. Ketelaar, "Investigation in the Infrared. I. The Absorption and Reflection Spectra of KHF_2 , KDF_2 , and RbHF_2 in Relation to the Bifluoride Ion," *Rec. trav. chim.*, 60, 523-55 (1941).

(2) G. Glockler and G. E. Evans, "The Double-Minimum Problem Applied to Potassium Hydrogen Fluoride," *J. Chem. Phys.*, 10, 607-9 (1942).

(3) J. A. A. Ketelaar, "The Infrared Absorption and Reflection Spectra of KHF_2 and KDF_2 ," *J. Chem. Phys.*, 9, 775-6 (1941).

(4) D. Polder, "Nature of the Hydrogen Bond in Potassium Hydrogen Fluoride," *Nature*, 160, 870-1 (1947).

and the calculations of Davies.⁽⁵⁾ More recently, in a complete thermodynamic study, Westrum and Pitzer⁽⁶⁾ showed that there is no residual entropy at absolute zero in the KHF_2 crystal and no specific heat anomaly above 15°K, which thus strongly supports the single potential minimum. In addition they suggested a reinterpretation of the infrared data which would support their conclusion.

This reinterpretation has been corroborated by Ketelaar⁽⁷⁾ who has very recently reported on polarized infrared studies of KHF_2 —a method which allows increased certainty in assignment of frequencies. The present neutron diffraction investigation was begun before the appearance of the latter two papers, but has been much delayed by certain experimental difficulties which will be discussed below. Even though the works of Westrum and Pitzer appear to be decisive, it seemed desirable to have confirmation of their conclusions by the essentially more direct method of a diffraction study. The results of such a study, which incidentally provides a more detailed knowledge of the structure and thermal motions of the bifluoride ion than is obtainable by other means, is presented below.

Powder Studies. The first attack on this problem by neutron diffraction was by spectrometer studies of powder samples. The spectrometer used

(5) M. Davies, "Simple Potential Functions for HF and $[\text{F-H}\cdots\text{F}]^-$," *J. Chem. Phys.*, 15, 739-41 (1947).

(6) E. F. Westrum and K. S. Pitzer, "Thermodynamics of the System KHF_2 -KF-HF, Including Heat Capacities and Entropies of KHF_2 and KF. The Nature of the Hydrogen Bond in KHF_2 ," *J. Am. Chem. Soc.*, 71, 1940-9 (1949).

(7) J. A. A. Ketelaar and W. Vedder, "The Infrared Spectrum of KHF_2 ," *J. Chem. Phys.*, 19, 654 (1951).

is similar to that described by Wollan and Shull,⁽⁸⁾ but is provided with the additional feature of automatic recording of data on strip charts. Monochromatic radiation of 1.16-A wave length obtained by reflection of a neutron beam from the (111) planes of a single crystal of copper was used in most of this work. Other patterns were obtained under other conditions.

Powder samples of both normal and deuterated potassium bifluoride were prepared for study. Reagent-grade potassium fluoride and hydrogen fluoride in equivalent quantity were directly reacted at room temperature in a platinum container. The resulting product was dried to constant weight at 100°C and analyzed for purity by titration with alkali. The several preparations made all contained less than 0.3% impurity. Several samples of the above material were deuterated essentially to completion by a process of repeated exchange with 99.8% D₂O. The reactions with D₂O were carried out in platinum or bakelite containers in either a controlled atmosphere or in a vacuum dessicator. Thus, the excess D₂O was distilled off in such a way as to prevent back exchange. Three or four repetitions of the process yielded products with deuterium contents of 90% or above. The deuterium contents were determined by density measurements on the recovered excess D₂O and by neutron transmission measurements on the final samples. The two methods gave excellent agreement.

The pure, dry samples were placed in tightly closed thin-walled cylindrical aluminum containers for diffraction measurements. The usual sample size was 1 cm in diameter and

5 cm in length, and required 3 to 4 g of material. The sample was rotated about the cylinder axis while the diffraction data were accumulated. Approximately 90 deg of scattering angle were covered, whereas scanning rates of 1 to 4 deg in 2 θ /hr were employed, depending on the degree of collimation that was introduced into the apparatus. Appropriately placed Soller slits, used when high resolution was desired, were capable of giving peak half-widths as narrow as 36 minutes of arc in the low angle region but only at a considerable sacrifice in intensity. Diffraction patterns were obtained on both normal and deuterated samples of KHF₂, but only the deuterated samples yielded much useful information. This is due to the larger coherent cross section of deuterium relative to hydrogen and to the very much lower diffuse scattering of deuterium, which results in far superior peak-to-background ratios. Diffraction data were also obtained for powdered nickel under identical conditions in order to allow conversion of intensities to structure factors on an absolute scale. Integrated intensities of the diffraction peaks were determined by measuring peak areas on the chart recording by use of a planimeter or alternatively by application of the trapezoid rule.

In spite of allowing data to accumulate over a long period, there is considerable uncertainty attached to many of the intensity values obtained because of very low intensities, inadequate resolution, and moderately high background levels. However, the diffraction peaks occurring at small angles are often well resolved and the intensities are often reproducible to within considerably better than 10%.

Preferred Orientation. Examination of the powder data showed that

⁽⁸⁾E. O. Wollan and C. G. Shull, "The Diffraction of Neutrons by Crystalline Powders," *Phys. Rev.*, 73, 830-41 (1948).

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reproducibility of some reflection intensities among different samples was not always within the expected limits. The particular peaks that seemed least reproducible also gave the poorest agreement with calculation for all reasonable models. A number of plausible explanations for this behavior, such as chemical or isotopic differences among the several samples, varying scattering behavior of the sample container, or instability in the counting circuits, were explored with negative results. Since KHF_2 is a soft crystal and crystallizes in thin plates, it seemed possible that preferred orientation induced by packing might be a plausible explanation. This hypothesis was

tested by obtaining data on samples packed in such a way as to minimize induction of orientation. Since no significant differences were observed in the new data, the above effects remained unexplained. More recently a further investigation of KHF_2 was made by the single crystal method and these data gave no indication of the same peculiarities. Another test for preferred orientation was then made, this time by obtaining diffraction patterns on KDF_2 , both with the sample in normal position and with the sample holder tilted 90 deg from the rotation axis of the counter in a plane perpendicular to the beam direction. The two patterns, shown in Fig. 11, illustrate the striking differences

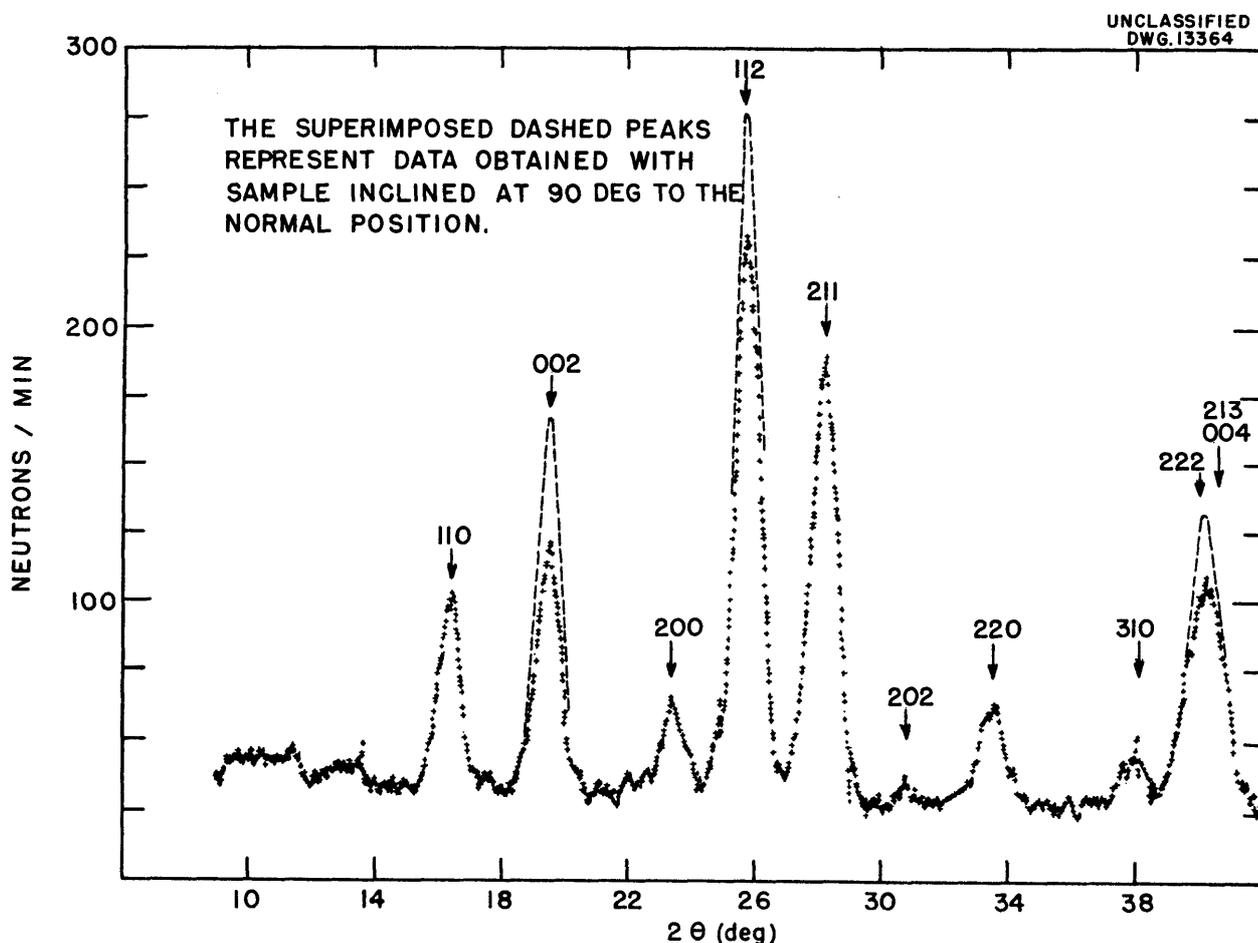


Fig. 11. Neutron Diffraction Pattern of KDF_2 .

found when this new test was made. The peaks particularly affected are (002) and (112), both of which had given experimental intensities that were low compared with calculation. If there is preferred orientation in the powder due to packing of thin plates with the c axis vertical, these planes with large l index are precisely the ones that should be affected. They would be expected to give abnormally low intensities with the cell in normal orientation and abnormally high intensities with the cell tilted 90 deg, as in the experiment. It seems quite clear that preferred orientation to an extent of 15 to 30% existed in the KHF_2 powder samples as prepared for the experiment.

Treatment of Data. While the presence of an indeterminate amount of preferred orientation in a sample does cast doubt upon the intensities obtained from such a sample, the actual data obtained did lead to the correct structure in the case of KHF_2 , as was confirmed by a single-crystal study reported below. Hence it is believed worthwhile to present the powder data obtained.

Experimental intensities corrected for background and sample-container scattering were converted to jF^2 values on an absolute basis by means of the standard X-ray equation fitted to the neutron case:

$$P_{hkl} = \left[\frac{I_0 V l \lambda^3}{8\pi r} \right] \frac{\rho'}{\rho} \frac{N^2 B_a}{\sin\theta \sin 2\theta} jF_{hkl}^2.$$

The notation follows the usual conventions. The quantity in parentheses, which is characteristic of the instrument, was evaluated from diffraction data on powdered nickel. The absorption correction B_a was evaluated from measured values of

the linear absorption coefficient for neutrons determined also at $\lambda = 1.16$ A. Calculated values of jF^2 were obtained by adaptation of the usual formula:⁽⁹⁾

$$F = \sum f_0 \cos 2\pi (hx + ky + lz).$$

The scattering amplitude f_0 is given by $(\sigma_{coh}/4\pi)^{1/2}$ as listed by Shull and Wollan⁽¹⁰⁾ for many substances.

X-ray studies of KHF_2 ^(11,12) have shown that the unit cell is tetragonal, with $a_0 = 5.67$, $c_0 = 6.81$, that the space group is D_{4h}^{18} , and that the atomic positions are K in the four-fold positions $(0, 0, 1/4)$ and F in the eight-fold positions $(u_F, \frac{1}{2} + u_F, 0)$ where $u_F = 0.1408$. Since it is extremely likely that the proton lies along the F - F bond, the logical location of the proton would also be an eight-fold $(u, \frac{1}{2} + u, 0)$ position. A model assigning one-half of a hydrogen atom in each of these positions would correspond to protons located at random in the two-potential-well model. If the parameter u is equal to zero, four-fold positions with hydrogen centered between the fluorine atoms would result. Since these are the only physically reasonable models they were the only ones carefully tested. Table 12 lists experimental jF^2 values from one of the more or less typical runs. Along with it are given corresponding jF^2 values for the parameter values $u = 0$ and $u = 0.035$. The latter parameter would

⁽⁹⁾International Tables for the Determination of Crystal Structure (Rev. ed.; Ann Arbor, Michigan: Edwards Bros., Inc., 1944).

⁽¹⁰⁾C. G. Shull and E. O. Wollan, "Coherent Amplitudes as Determined by Neutron Diffraction," *Phys. Rev.*, 81, 527 (1951).

⁽¹¹⁾R. M. Bozorth, "The Crystal Structure of Potassium Hydrogen Fluoride," *J. Am. Chem. Soc.*, 45, 2128-35 (1923).

⁽¹²⁾L. Helmholtz and M. T. Rogers, "A Redetermination of the Fluorine-Fluorine Distance in Potassium Bifluoride," *J. Am. Chem. Soc.*, 61, 2590-2 (1939).

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Table 12

Powder Diffraction Data from KDF_2

hkl	jF^2 EXPERIMENTAL	jF^2 CALCULATED $u = 0$	jF^2 CALCULATED $u = 0.035$
110	26.2	24.8	22.8
002	40.2	47.4	47.4
200	28.4	25.2	21.7
112	169.0	193.6	187.0
211	152.5	150.4	168.0
202	5.7	0.2	1.0
220	47.1	43.2	34.6
310	20.2	20.5	36.0
222	5.5	3.3	0.8

Note: f_D was taken as 0.56 since the sample was 92% deuterated. Only data from resolved peaks are presented.

correspond to a separation between the two proton locations of 0.56 Å. Temperature factors used correspond to those found in the single-crystal work reported below, including the asymmetry to be discussed. The agreement obtained for the zero parameter is definitely better than that for $u = 0.035$. Careful examination of the data indicates the correct parameter value to be less than 0.02. This result corresponds to a separation between proton positions of less than 0.39 Å. Thus the powder data give a result that has some significance in establishing the central hydrogen location. The single-crystal data will be seen to set closer limits on the proton location.

Single-Crystal Work. Recent work⁽¹³⁾ has shown that at least in some cases crystal-structure factors

can be accurately determined by means of single-crystal neutron-diffraction measurements. Accordingly single crystals of KHF_2 were prepared by slow evaporation of (ordinary) aqueous solutions of the purified salt. A specimen that had approximate dimensions of 1.8 x 2.4 x 3.5 mm was selected for study. A rough calculation was made based on Bacon and Lowde's⁽¹⁴⁾ criterion for the limiting thickness of crystal that should display little or no extinction in the strong (211) reflection. This yielded a limiting thickness of 2.1 mm on the assumption of a mosaic-spread parameter of 5 minutes. The crystal was mounted on an adjustable goniometer head and adjusted until a (110) zone axis, and later a (100) zone axis, was accurately vertical. Integrated reflections were obtained from the various planes by rotating the crystal through the reflection

(13) S. W. Peterson and H. A. Levy, "The Use of Single Crystal Neutron Diffraction Data for Crystal Structure Determination," *J. Chem. Phys.*, 19, 1416 (1951).

(14) G. E. Bacon and R. D. Lowde, "Secondary Extinction and Neutron Crystallography," *Acta Cryst.*, 1, 303-14 (1948).

angle and simultaneously rotating the detector at twice the angular velocity of the crystal. Tests were made to ensure that the entire Bragg reflection entered the detector. The angular velocity of rotation of the crystal was usually 8 deg/hr. The peak was recorded on a strip-chart recorder and at the same time the total accumulated number of counts as indicated by a scalar was recorded. The integrated peak intensity was taken to be the total number of counts entering the detector during the scanning period, corrected for the background radiation as observed when the crystal was just out of reflecting position. Individual reflections were found to be reproducible to a few per cent.

Structure factors were obtained from the integrated intensity data by application of the following equation adapted from the standard X-ray expression:⁽¹⁵⁾

$$E_{hkl} = \left[\frac{I_0 \lambda^3}{\omega} \right] \frac{N^2 V B_a F_{hkl}^2}{\sin 2\theta} .$$

In order to obtain absolute values of F , the instrumental constants $I_0 \lambda^3 / \omega$ were evaluated by making use of data from a NaCl crystal that has previously been carefully studied.⁽¹⁶⁾ Absorption corrections were estimated from a measured value for the linear absorption coefficient of KHF_2 , using a cylindrical approximation for the crystal shape. Experimental F values were compared with structure factors calculated for the models described above. The first step involved calculating structure factors for several values of the parameter u without applying temperature factors. The

over-all fit at this stage was very poor for any of the parameter values, and it was quite apparent that application of a single over-all Debye-Waller temperature factor would be of little value. Hence separate temperature factors were introduced for each of the atoms, and systematic variation of these led to much improved agreement. Careful examination of the data at this stage brought out the fact that planes with a large l index were being calculated consistently too large. This, it may be recalled, is similar to the effect ascribed to preferred orientation in the powder data but of a smaller order of magnitude. The possibility of an explanation of this effect in terms of special temperature motions for the hydrogen atom was explored with essentially negative results. It was finally discovered that application of an asymmetric temperature factor to the fluorine atoms, similar to that applied by Lely and Bijvoet⁽¹⁷⁾ to the CN group in NH_4CN , was exactly what was needed to bring calculated and experimental structure factors into excellent agreement. The asymmetric temperature factor used was of the form

$$e^{-(B_1 + B_2 \sin^2 \alpha) (\sin \theta / \lambda)^2} ,$$

where α is the angle between the normal to the reflecting plane and the c axis of the crystal. The coefficient B_1 applies to the spherically symmetrical component of temperature vibration, whereas B_2 applies to the asymmetric component. Suitability of such a temperature factor and the values of B_1 and B_2 found imply greater motion of the fluorine atoms in the $a - b$ plane and suggest a torsional oscillation of the bifluoride ion.

⁽¹⁵⁾International Tables for the Determination of Crystal Structure, *op. cit.*

⁽¹⁶⁾S. W. Peterson and H. A. Levy, *op. cit.*

⁽¹⁷⁾J. A. Lely and J. M. Bijvoet, "Crystal Structure and Anisotropic Temperature Vibration of NH_4CN ," *Rec. trav. chim.*, 63, 39-43 (1944).

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Table 13

Single-Crystal Diffraction Data from KHF_2

hkl	F EXPERIMENTAL	F CALCULATED $u = 0$	F CALCULATED $u = 0.02$	hkl	F EXPERIMENTAL	F CALCULATED $u = 0$	F CALCULATED $u = 0.02$
110	1.16	1.16	1.13	332	2.70	2.64	2.77
002	1.37	1.30	1.30	215	2.10	2.12	2.15
200	0.93	0.96	0.92	422	1.45	1.49	1.35
112	1.59	1.50	1.52	006	0.53	0.54	0.54
211	3.08	3.06	3.10	116	1.21	1.19	1.20
202	3.40	3.43	3.39	334	0.40	0.22	0.32
220	0.29	0.10	0.18	206	2.39	2.34	2.31
222	2.39	2.35	2.27	424	0.59	0.71	0.83
004	3.49	3.44	3.44	440	2.56	2.62	2.81
213	2.64	2.70	2.74	325	1.10	1.14	1.20
114	1.10	1.05	1.03	226	1.67	1.67	1.62
321	1.60	1.65	1.76	442	0.25	0.52	0.69
204	0.62	0.59	0.55	600	1.80	1.75	1.94
400	3.28	3.15	3.01	062	0	0.22	0.04
330	0.53	0.44	0.58	046	3.32	3.41	3.33
402	5.04	5.23	5.10	008	1.99	1.97	1.97
224	0.15	0.23	0.30	064	1.48	1.49	1.64
323	1.48	1.46	1.55	550	1.21	1.19	1.01
420	0.79	0.73	0.88				

For purposes of calculation the above formula was put in the form

$$e^{-B_1 (\sin \theta/\lambda)^2} e^{-B_2 (l/2c)^2}$$

Table 13 lists experimental and calculated structure factors for two parameter values for the 37 reflections examined. In spite of the apparent excellence of the agreement with a parameter value of zero, it was found that the parameter could be determined to a precision of only ± 0.01 . This is due primarily to broadening of the parameter-sensitive

high-index reflections, because the incident radiation is not strictly monochromatic and results in inferior peak-to-background ratios—hence, less precise data.

Results and Conclusions. The hydrogen parameter is determined by this investigation to be less than 0.01, which limits the distance between proton positions to less than 0.195 Å or indicates the proton to be within 0.098 Å of the center of the $F-F$ bond. This may be taken as confirmation of the result of Westrum and Pitzer. The Debye temperature-factor coefficients were found to be

$B_K = 1.25$, $B_H = 3.0$, $B_{1F} = 1.85$, and $B_{2F} = 1.0$. These correspond to root-mean-square displacements of 0.13, 0.20, 0.15, and 0.11 Å for the respective atoms. The asymmetric temperature coefficient found for the bifluoride ion may indicate an approach toward rotation, and it may possibly be related to the known high-temperature phase of KHF_2 .⁽¹⁸⁾

SINGLE-CRYSTAL NEUTRON CRYSTALLOGRAPHY

An empirical study of neutron diffraction from single crystals of sodium chloride was reported in the preceding quarterly report.⁽¹⁹⁾ These measurements indicated that the intensities of Bragg reflections conformed to the simple ideal crystal law ($E\omega/I_0 = QV$) for specimens several millimeters in dimension and thus of ample size for practical experimental use. This result is in conflict with Bacon and Lowde⁽²⁰⁾ who concluded from theory that because of secondary extinction specimens would have to be kept smaller than about 0.1 mm to conform to this simple law.

This study has been extended by comparing a few structure factors measured from single-crystal intensities of a number of substances with those measured from the usual powder intensities. Agreement of the two methods indicates conformity to the simple law. The results are presented in Table 14. Calculated structure factors without temperature corrections are also listed for most of the crystals. Approximate corrections for absorption in the single crystals were estimated, treating each specimen as that cylinder parallel

to the rotation axis that most nearly approximated its actual form. The corresponding correction was applied to the NaCl data used as standard to establish the absolute scale. The usual absorption corrections were applied to the powder data. Good agreement is obtained for KCl, KBr, KHF_2 , and NH_4Cl , whereas LiF, CaCO_3 , and CaF_2 show deviations probably assignable to extinction in the single crystal. These last three materials are known to crystallize with a high degree of perfection.

Also listed in Table 14 are calculated limiting thicknesses for a number of the reflections according to Bacon and Lowde's thin-crystal criterion. The formula was applied for the case of symmetrical transmission and the cosine of the angle of the incident beam with respect to the normal to the surface was taken as unity. The low value of 5 ft has been assigned to the mosaic-spread parameter for all specimens in the absence of more detailed knowledge. These calculated thicknesses should be roughly applicable to specimens differing from parallel plates if compared to the maximum dimension in the section parallel to the incident and scattered beams. The values of this dimension for the specimens used (also listed in the table) are in general larger than the thin-crystal limit even in those cases that gave little or no extinction. However, considering that the mosaic spreads may be larger by a factor of two or three than that assumed, this does not invalidate the theoretical criterion of Bacon and Lowde, but indicates that they were unduly pessimistic in its application. In any case, it is apparent that the limiting thickness of 0.1 mm postulated by Bacon and Lowde does not have any general significance, and that in many cases it is possible to use crystals with

⁽¹⁸⁾E. F. Westrum and K. W. Pitzer, *op. cit.*

⁽¹⁹⁾H. A. Levy and S. W. Peterson, "Neutron Diffraction Studies," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951*, ORNL-1116.

⁽²⁰⁾G. E. Bacon and R. D. Lowde, *op. cit.*

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Table 14

Comparison of Structure Factors from Single-Crystal and Powder Measurements

SUBSTANCE	INDICES	STRUCTURE FACTOR $\times 10^{12}$			THIN CRYSTAL LIMIT ^(b) (mm)	THICKNESS ^(c) (mm)
		OBSERVED FROM POWDER	OBSERVED FROM SINGLE CRYSTAL	CALCULATED ^(a)		
KBr	(111)	1.29	1.27	1.28	1.6	1.9
	(200)	4.04	4.09	4.08		
KCl	(111)	2.40	2.37	2.56	0.7	1.8
	(200)	5.04	4.71	5.36		
KHF ₂	(121)	3.09	3.08	3.06 ^(d)	2.3	2.8
NH ₄ Cl	(110)	1.34	1.27	-	0.8	2.0
LiF	(111)	2.80	1.63	2.92	0.2	1.8
	(200)	1.51	1.04	1.48		
	(400)	1.49	1.19	1.48		
CaF ₂	(111)	1.74	1.57	1.95	0.4	1.7
	(200)	2.45	2.13	2.44		
	(220)	6.17	3.17	6.36		
CaCO ₃	(211) ^(e)	3.29	2.39	3.46	0.5	1.6

(a) No temperature correction included except as noted.

(b) According to the "thin-crystal" criterion of Bacon and Lowde.

(c) Approximately the largest dimension of the specimen in the section normal to the rotation axis.

(d) Includes temperature factors.

(e) Cleavage plane. Indices and structure factor based on primitive rhombohedral unit.

thicknesses in the millimeter range for structural work.

In addition to the foregoing data, a large number of intensities from a single crystal of KHF₂ are reported in the preceding section of this report. The excellent agreement between experimental and calculated structure factors for the complete list of reflections examined, with no extinction corrections, is additional strong evidence that extinction is not a serious problem in many crystal specimens of moderate size.

It may be concluded that single-crystal neutron reflections should be

useful for structure determinations in many cases. Inherent advantages of the method include greatly increased resolution and greatly reduced sample size. A corollary to the latter feature is that incoherent scattering is greatly reduced relative to the intensity of Bragg reflections; this will be of great importance in crystals containing hydrogen and will make unnecessary the preparation of the deuterated specimens usually required in the powder method. It is clear that many relatively complex crystals, including those containing several hydrogen atoms, are now open to attack by neutron diffraction.

An account of this work has been published.⁽²¹⁾

WORK IN PROGRESS

Ammonium Chloride. Powder data from deuterio-ammonium chloride, and single-crystal data from ordinary ammonium chloride, show clearly that the structure reported recently by Goldschmidt and Hurst⁽²²⁾ for the room-temperature phase of this substance is incorrect. The correct structure is a disordered one similar to that of room-temperature ammonium bromide.⁽²³⁾ A complete account of this work is in preparation.

Vitreous Silica (with W. O. Milligan, Rice Institute). Arrangements have been made with the Mathematics Panel for machine computation of radial-distribution integrals. One such integral, incorporating a convergence factor, has been completed to supplement previous computations carried out in Houston. This work will be described in a later report.

Palladium and Platinum Oxides (with J. Waser, Rice Institute). Neutron-diffraction data from palladium oxide appear to confirm the structure deduced from X-ray data by Moore and Pauling.⁽²⁴⁾ Platinum oxide yielded a pattern with extremely broad lines that is quite difficult to interpret. Treatment of the data is being continued by J. Waser in Houston.

⁽²¹⁾S. W. Peterson and H. A. Levy, *op. cit.*

⁽²²⁾G. H. Goldschmidt and D. G. Hurst, "The Structure of Ammonium Chloride by Neutron Diffraction," *Phys. Rev.*, 83, 88 (1951).

⁽²³⁾H. A. Levy and S. W. Peterson, "The Nature of the Second-Order Transition in ND_4Br ," *Phys. Rev.*, 83, 1270 (1951).

⁽²⁴⁾W. J. Moore, Jr., and Linus Pauling, "The Crystal Structures of the Tetragonal Monoxides of Lead, Tin, Palladium, and Platinum," *J. Am. Chem. Soc.*, 63, 1392-4 (1941).

Potassium Dihydrogen Phosphate (with J. Worsham). Single-crystal data from two specimens of KH_2PO_4 have been collected. Comparison with two powder reflections that could be resolved indicates that the single crystal intensities are severely reduced by extinction. Considerable improvement was achieved by chilling a specimen in liquid nitrogen; this procedure presumably increased the mosaic character of the specimen. The investigation is continuing.

EXPERIMENTS IN CHEMICAL KINETICS WITH MOLECULAR BEAMS

S. Datz E. H. Taylor

During this period some difficulties were encountered with the surface-ionization gage. After redesign it functioned satisfactorily in tests on a beam of KBr. The improved performance of the gage revealed some weaknesses in the present over-all arrangement, and it is being modified. In the meantime, experiments are going forward on simpler separation and counting methods for the radiobromine obtained by neutron activation.

RADIO-FREQUENCY SPECTROSCOPY

R. Livingston

Pure Quadrupole Spectra

Pure quadrupole spectra studies have been continued on a variety of chlorine compounds. The desirability of making measurements at liquid-hydrogen (20°K) and liquid-helium (4°K) temperatures was discussed in the last quarterly report.⁽²⁵⁾ All the liquid-nitrogen (77°K) temperature observations on the chloromethanes have been repeated at 20°K , and a

⁽²⁵⁾R. Livingston, "Radio-Frequency Spectroscopy," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951*, ORNL-1116.

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Table 15

Observed Frequencies and Quadrupole Couplings for Chlorine-35

COMPOUND	OBSERVED FREQUENCY (mc)			$ e\phi Q $ avg. (mc) 20°K
	77°K	20°K	4°K	
CH ₃ Cl	34.029	34.199	34.206	68.40
CH ₂ Cl ₂	35.991	36.233	36.243	72.47
CHCl ₃	38.254	38.486		76.98
CCl ₄	38.308	38.490		81.85
	40.46*	41.139		
	40.52	41.109		
	40.54	41.045		
	40.61	41.022		
	40.64	40.972		
	40.65	40.965		
	40.72	40.918		
		40.895		
		40.888		
		40.831		
		40.826		
		40.800		
		40.794		
	40.732			
CHF ₂ Cl		35.249		70.50
CF ₃ Cl	38.089	38.790		77.58
CHFC1 ₂	36.479	36.752		73.53
	36.508	36.775		
CF ₂ Cl ₂	38.450	39.078		78.16
CFC1 ₃	39.161	39.537		79.63
	39.517	39.867		
	39.703	40.046		
CF ₂ BrCl	38.342	38.675		77.35
Cl ₂	54.248	54.476**		108.95

*Fourteen, very weak, closely spaced lines were observed. Approximate frequencies are given for seven of them.

**The chlorine-37 frequency was measured at 20°K, and that for chlorine-35 was computed from the quadrupole-moment ratio. Both isotopes were measured at 77°K and the ratio agreed with the published value.

few observations were repeated at 4°K. In addition many new measurements have been made.

Table 15 summarizes all quadrupole-coupling data now complete on the solid substituted methanes and on

molecular chlorine. This table and an interpretation of the coupling changes as outlined in the last quarterly report have been published.⁽²⁶⁾

⁽²⁶⁾H. J. Barber, "Cuprous Cyanide—Its Preparation and Use," *J. Chem. Soc.*, 79 (1943).

The spin-system coupling with lattice vibrations is responsible for the frequency change with cooling and also the relaxation mechanism. Cooling from 77 to 20°K produces a small frequency (quadrupole-coupling) increase, whereas further cooling to 4°K, in those few cases studied, gives only a minor additional increase. A preliminary measurement on CHCl_3 at 4°K gave similar results. This indicates that lattice vibrations are quite effectively frozen out at 20°K. The sensitivity of the equipment was noticeably improved in cooling from 77 to 20°K, due to a more favorable Boltzmann distribution of energy levels, but at 4°K the sensitivity decreased greatly. Presumably the improved Boltzmann factor at 4°K is more than compensated for by an increase in relaxation time, giving a net loss in sensitivity. This is in keeping with the observation that lattice vibrations are quite thoroughly frozen out at 4°K.

Coupling values for chlorine, spin 3/2, have always been computed by multiplying the observed transition frequency by two. This is exact only for the case of an axially symmetric field-gradient system. J. Jauch, during his summer visit at this Laboratory, and J. Goldstein (independently) have worked out the energy levels for a quadrupolar nucleus in an asymmetric field-gradient system. For the spin 3/2 case the final expression for the transition energy is

$$E = \frac{\alpha}{2} \left[1 + \frac{\beta^2}{3\alpha^2} \right]^{1/2},$$

where $\alpha = eQ\phi_{ZZ}$, and $\beta = eQ(\phi_{XX} - \phi_{YY})$. For axial symmetry $\phi_{XX} = \phi_{YY}$, hence, $\beta = 0$ and the transition energy is $eQ\phi_{ZZ}/2$. Keeping in mind that the gradients obey Laplace's equation it is easily demonstrated that even

with a relatively marked asymmetry in the field-gradient system the error introduced is small in taking the coupling as twice the transition frequency. Observations on vinyl chloride in collaboration with J. Goldstein of Emory University will appear as a Letter to the Editor in the *Journal of Chemical Physics*. The transition frequency for chlorine-35 at 77°K is 33.414 mc and at 20°K is 33.613 mc. Taking twice the frequency gives a coupling of approximately (-)67 mc. The asymmetry in the field-gradient system is known for vinyl chloride, from microwave measurements,⁽²⁷⁾ to be $\beta = -7$ mc. This would lead to an apparent value of (-)67.1 mc for α . Thus the effect of asymmetry is in this case quite negligible. In the analysis of the microwave data a value of -67 ± 2 mc was obtained for $eQ\phi_{ZZ}$ by assuming the C-Cl bond in this asymmetric top molecule to be a principal axis of the field-gradient tensor. The good agreement with the present value indicates that the above assumption is a reasonable one. The above-mentioned Letter to the Editor will also contain the Hamiltonian and matrix elements needed to determine the energy levels for other spin cases.

Quadrupole transitions for ClF and ClF_3 have been determined in a cooperative effort with D. F. Smith of K-25. Special cells were developed to withstand the corrosive action of the compounds and to allow measurements to be made at higher frequencies than usually used. Observations were unsuccessful at 77°K but were successful at 20°K. The chlorine-35 line in ClF appears at 70.7000 mc. The chlorine-37 line was also observed at 55.7129 mc, but was so weak that

(27) J. H. Goldstein and J. K. Bragg, "Nuclear Quadrupole Effects in the Microwave Spectrum of the Asymmetric-top Molecule, Vinyl Chloride," *Phys. Rev.*, 75, 1453-4 (1949).

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the frequency measurement is not as accurate as that for chlorine-35. Nevertheless, the computed quadrupole-moment ratio, 1.26901, is in fairly good agreement with the previously determined value of 1.26878 ± 0.00015 . The chlorine-35 frequency in ClF_3 is 75.1295 mc and the chlorine-37 value is 59.2147 mc. Here the quadrupole-moment ratio, 1.26876, is in excellent agreement with the above value. The full width of the chlorine-35 line at half maximum was estimated as 7 kc. These substances should have the highest quadrupole couplings of any known chlorine compounds.

Several additional studies have been made at 20°K. The chlorine-35 transition in HCl was not previously found at 77°K, but has been found at 20°K as a very broad line at 26.695 ± 0.008 mc. The four chlorine-35 lines in SiCl_4 appear at 20.370, 20.501, 20.521, and 20.552 mc. In AsCl_3 two lines appear at 25.048 and 25.158 mc. A third line, not previously seen in the 77°K measurements, appeared at 25.520 mc. The measurements at 77°K have not yet been repeated to check on the third line. The quadrupole spectra for nitrogen-14 have been sought in solid NH_3 and solid N_2 at 20°K in the region of 3 mc, but they have not been found. It will probably be necessary to improve the spectrometer sensitivity before nitrogen-14 spectra are observed. Also, the chlorine-35 transitions in CH_2ClBr and CHBrCl_2 have been unsuccessfully sought at 20°K.

A number of interesting comparisons can now be made between the quadrupole data determined on the solids reported here and measurements made elsewhere. All new cases of the determination of the quadrupole-moment ratio of chlorine-35 and chlorine-37 reported here have given values in good agreement with the earlier re-

ported value of 1.26878. At the time of reporting, this value⁽²⁸⁾ was in disagreement with Dehmelt and Krüger's value of 1.2661 determined in solid trans-dichloroethylene, and the atomic beam value of 1.2795. Recently Dehmelt and Krüger⁽²⁹⁾ have published a more accurate value of 1.2688 which was found in solid trans-dichloroethylene. Also the atomic beam measurements were repeated⁽³⁰⁾ and an error was found in the chlorine-35 coupling. The new ratio is 1.2686 ± 0.0004 . There, however, remain several cases of determinations of the ratio by the microwave method⁽³¹⁾ on gaseous molecules that seem to depend on the nature of the molecule. The earlier reported coupling for chlorine-35 in solid molecular chlorine at 77°K was found to be (-)108.5 mc, as compared with the old atomic beam value of -110.4 mc. The striking similarity indicated that molecular chlorine has a bond that uses essentially a pure *p* orbital.⁽³²⁾ The new coupling for Cl_2 at 20°K, given in Table 15, is a more suitable one for making the comparison, since lattice vibrations have been more effectively frozen out. This value, (-)108.95 mc, is only 0.7% lower than the remeasured atomic beam value of -109.7 mc. The coupling in solid CF_3Cl (Table 15) is 0.6%

(28) R. Livingston, "The Quadrupole Moment Ratio of Chlorine-35 to Chlorine-37 from Pure Quadrupole Spectra," *Phys. Rev.*, 82, 289 (1951).

(29) H. G. Dehmelt and H. Krüger, "Quadrupol-Resonanzfrequenzen von Cl- und Br-Kernen in Kristallinen Dichlorethylen und Methylbromide," *Z. Physik*, 129, 401 (1951).

(30) V. Jaccarino and J. G. King, "On the Ratio of the Nuclear Magnetic and Electric Quadrupole Interactions of Atomic Chlorine-35 and Chlorine-37," *Phys. Rev.*, 83, 471 (1951).

(31) S. Geschwind, R. Gunther-Mohr, and C. H. Townes, "Ratio of the Quadrupole Moments of Chlorine-35 and Chlorine-37," *Phys. Rev.*, 81, 288 (1951).

(32) R. Livingston, "The Pure Quadrupole Spectrum of Solid Chlorine," *J. Chem. Phys.*, 19, 803 (1951).

lower than the microwave value.⁽³³⁾ On the other hand, the value for CH_3Cl is 9.0% lower than the microwave value of 75.13 mc.⁽³⁴⁾ This is much like Dehmelt and Krüger's values for bromine in solid CH_3Br , which is 8.3% lower than the microwave value, and for iodine in CH_3I , which is 9.3% low.⁽³⁵⁾ The value in CH_2Cl_2 (Table 15) is 7.1% lower than the recent microwave value of -78.0 ± 2 mc.⁽³⁶⁾ These differences in the substituted methanes seem to be indicative of a change in character of the carbon-halogen bond on going from the gaseous to the solid state. The above-reported frequency for chlorine-35 in ClF gives a coupling of $(-)\text{141.40}$ mc which is 3.1% lower than the microwave value of -145.99 mc.⁽³⁷⁾

A NEW TYPE OF SPECTRUM IN CRYSTALLINE SOLIDS

In the course of searching for quadrupole transitions in a large variety of chlorine compounds, a few substances were found that gave a very complex new type of spectrum. The interpretation is far from complete, but of the many possibilities considered several have been experimentally ruled out. Generally the new spectra consist of a very large number of closely spaced lines extending in frequency over the entire range of the equipment. So far no

uniformity in trend or structure has been found in the spacing of the lines or in the relative intensities, which vary over wide limits.

Several observations indicated that these new lines were not associated with nuclear spin orientations as in the case of the pure quadrupole spectra. The most direct experimental demonstration of this was the finding that the new lines were insensitive to an applied magnetic field. On the other hand, all pure quadrupole spectra lines are greatly perturbed by a weak magnetic field. In the present experimental equipment, using substances that are not single crystals, the magnetic field causes the quadrupole lines to broaden and disappear. An experiment carried out on the pure quadrupole spectra lines of CHCl_3 showed a field of 12 gauss to be sufficient to broaden the line so that it could no longer be seen. Whenever quadrupole lines are now observed they are always tested by using a magnet. If a single crystal were used in a homogeneous magnetic field, the quadrupole lines would displace in frequency.

The observations are far from complete but the general details on each of the substances studied are summarized below. Solid NH_3 at 77°K gives extremely strong sharp lines over all tuning ranges so far searched. These ranges are 2.6 to 7.0 mc and 16 to 38 mc. About 90 lines were counted in the 37.0-to 38.0-mc range, which gives an estimate of 2000 lines for the 16-to 38-mc range alone. The intensities varied over wide limits in what appeared to be a random manner. The lines in solid NH_3 at 77°K are not stable, and they gradually broaden and disappear. An experiment was carried out in which the sample was held at 77°K overnight, and during that time the lines disappeared. The sample was then slowly warmed to the

(33)D. K. Coles and R. H. Hughes, "Microwave Spectrum of CF_3Cl ," *Phys. Rev.*, 76, 858 (1949).

(34)W. Gordy, J. W. Simmons, and A. G. Smith, "Microwave Determination of the Molecular Structures and Nuclear Couplings of the Methyl Halides," *Phys. Rev.*, 74, 243-9 (1948).

(35)H. G. Dehmelt, "Kernquadrupolfrequenzen in Kristallinen Jodverbindungen," *Naturwissenschaften*, 37, 398 (1950).

(36)W. D. Gwinn and R. J. Myers, Ohio State University Symposium on Molecular Structure and Spectroscopy, June 13, 1951.

(37)D. A. Gilbert, A. Roberts, and P. A. Griswold, "Nuclear and Molecular Information from the Microwave Spectrum of FCl ," *Phys. Rev.*, 76, 1723 (1949).

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melting point of NH_3 . The experiment will have to be repeated with a slower and more controlled temperature change, but in this first crude experiment the lines started to appear at roughly -165°C , disappeared at roughly -143°C , reappeared at -138°C , finally broadening and disappearing as the melting point was approached. The lines in NH_3 have been observed in three independent experimental arrangements.

NH_4Cl was observed in the general range of 21 to 38 mc. It gave lines very similar to those in solid NH_3 . These lines quickly disappeared at -196°C (20 min), but they reappeared and seemed quite stable over several hours at dry ice temperature (-78°C). They were not present at room temperature. A sample was cooled from room temperature to -160°C in a crude experiment, and the appearance and disappearance of lines was noted. Lines first appeared at -57°C . It is not unlikely that more controlled experiments will show this to be at about -31°C , the lambda-point temperature for NH_4Cl . The lines disappeared at -160°C . It is quite possible that more careful work will show the transition at -140°C . At this temperature it has been observed that the proton magnetic-resonance line width suddenly changes.⁽³⁸⁾ NH_4Cl is now under study by neutron-diffraction methods by Levy and Peterson, and it is hoped that additional information on the structures at various temperatures will be available soon.

Similar lines have been observed in CF_2Cl_2 over the range 25 to 48 mc at 20°K . In this case the chlorine quadrupole lines were also observed and were normal.

⁽³⁸⁾H. S. Gutowsky and G. E. Pake, "Nuclear Magnetism in Studies of Molecular Structure and Rotation in Solids: Ammonium Salts," *J. Chem. Phys.*, 16, 1164-5 (1948).

The lines have been seen in SiHCl_3 over the entire range of about 10 to 33 mc. At 77°K they are very broad and weak. Over the range of 18 to 33 mc, 525 of the broad lines were counted. Cooling to 20°K caused the lines to become sharper and stronger, and a corresponding increase in the number was seen. The sample was not maintained at 20°K long enough to see whether the spectrum was stable.

ClF_3 showed very weak lines at 20°K over the approximate range of 59 to 80 mc. NH_4Br did not show the effect.

Solid CH_3Cl showed a 41-line spectrum at 20°K over the frequency range 21.4 to 42 mc. It has not been possible to repeat this observation. On one occasion CH_3Cl at 77°K showed a single line at 35.0 mc. The experiment was repeated several times, but in no case was the line found again. Two experiments were made on CH_3Cl at 4°K and in both cases weak lines were seen in the region of 40 mc. It is possible that CH_3Cl may show the many-lines spectrum at higher temperatures. This experiment will be done soon.

In all cases the lines move to lower frequency as the sample is warmed.

CALORIMETRY OF RADIOACTIVITY

G. H. Jenks

As discussed in previous quarterly reports, the power generated by a given amount of carbon-14 is being determined in order to establish a tie-in between the half-life and the average beta energy of the carbon-14 decay. The determination required measurements on a mixture of C^{14}O_2 and C^{12}O_2 of the heat liberated by a given amount of mixture and the abundance of C^{14}O in the mixture.

The thermal measurements were completed some time ago and have been reported.^(39,40) The concentration determination, which was carried out by measuring the density of the mixture relative to that of normal CO₂ by means of a small gas-density balance, has now been completed. These measurements are described briefly below.

MEASUREMENT OF THE C¹⁴O₂ CONCENTRATION IN A C¹⁴O₂-C¹²O₂ MIXTURE

Relative densities are measured with a gas-density balance by comparing the buoyancy of a reference gas with the buoyancy of the gas under investigation. This is usually accomplished by maintaining the balance and surrounding gas at a given constant temperature and measuring the pressure required to float the balance to a given position for each gas. In the present case the difference to be expected between the densities of the gas mixture and that of normal CO₂ was about 1%. Because of the limited size of the samples (0.76 ml STP in one case), it was necessary to operate the balance at a reduced pressure of about 100 mm Hg. Thus, if the difference in balancing pressures was to be measured to within 1%, it would be necessary to measure the total pressure to 0.01 mm, a precision which would be difficult to attain. However, the maintenance of a given pressure to better than this precision is readily accomplished by methods developed in connection with the calorimetric program.⁽⁴¹⁾ In view of this, the

method adopted in the present case was that of holding the pressure rather than the temperature constant and measuring the temperature at which the balance floated in a given position.

Apparatus. The gas-density balance constructed for these measurements was similar to the balance described by Aston.⁽⁴²⁾ It was made of silica glass, and was about 5 cm in length with a bulb volume of about 1 ml. The sensitivity of the balance was adjusted so that a change in buoyant force of 4.5×10^{-8} g resulted in a change of 0.1 mm in the position of the balance tip.

The pressure-controlling device was similar to those previously used and described by this group,⁽⁴³⁾ but a modification was made in the method of sensing the level of the mercury column. A metallic plate was placed about 1 mm above the mercury surface, and the capacitance between the two surfaces was included in a resonance circuit. Variations in the level of the mercury produced variations in resonance frequency that were detected and converted into a d-c output by a discriminator. The complete sensing element was designed and constructed by B. M. Hilderbrant of the Instrument Department.

The gas-handling system had provision for introducing samples of the gases of which the buoyancies were to be measured, for purifying the gases by fractional distillation, for measuring the volume of samples, and for storage. Mercury cut-off valves were used throughout.

(39) G. H. Jenks and F. H. Sweeten, "Calorimetry of Radioactivity," *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1950*, ORNL-1036, p. 60.

(40) *Ibid.*, ORNL-1053, p. 112.

(41) C. V. Cannon and G. H. Jenks, "A Microcalorimeter Suitable for Study of Easily Absorbed Nuclear Radiations," *Rev. Sci. Instruments*, 21, 236-40 (1950).

(42) F. W. Aston, "Simple Form of Microbalance for Determining the Densities of Small Quantities of Gas," *Proc. Roy. Soc. London*, (A) 89, 439-46 (1913).

(43) C. V. Cannon and G. H. Jenks, *op. cit.*

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Purification of Gas Samples. The $C^{14}O_2-C^{12}O_2$ mixture from which the samples for the gas-density measurements were taken was produced by thermal decomposition of $BaCO_3$. Prior to the decomposition, the $BaCO_3$ was outgassed at $500^\circ C$. The maximum temperature reached in the decomposition was $1100^\circ C$. Normal CO_2 for use as the reference gas was produced by decomposing outgassed $NaHCO_3$ at $250^\circ C$. The water that is also produced in the latter decomposition was removed by passing the gas at 600-mm pressure through a dry ice trap.

Before each measurement of the buoyancy for a given gas, the gas was purified by two procedures: (1) by evacuating a trap in which the CO_2 was frozen at $-196^\circ C$, and (2) by distilling the CO_2 from a trap held at $-150^\circ C$. Low-boiling gases such as air and CO

were removed in step 1, and higher boiling substances such as water were removed in step 2. Measurements and purifications on each gas were repeated until the buoyancy of the gas remained constant.

Results. Two different samples of the $C^{14}O_2-C^{12}O_2$ mixture were measured. The balancing temperatures determined for these samples and for the reference gas are shown in Table 16, together with values for percentage $C^{14}O_2$ concentrations computed from the balancing temperatures. A difference in the pressures at which the two samples were measured accounts for the difference in balancing temperatures for normal CO_2 .

A final evaluation of the method followed in the density measurement and the results has not yet been made.

Table 16

Balancing-Temperature Data

SAMPLE NO.	BALANCING TEMPERATURE ($^\circ K$)		$C^{14}O_2$ CONCENTRATION (%)
	NORMAL CO_2	$C^{14}O_2-C^{12}O_2$ MIXTURE	
1	299.875	302.941	22.58
2	300.315	303.365	22.44

RADIATION CHEMISTRY

RADIATION CHEMISTRY OF AQUEOUS REACTOR SOLUTIONS

J. A. Ghormley T. J. Sworski
C. J. Hochanadel

The radiation chemistry of aqueous uranyl sulfate, uranyl fluoride, and other proposed reactor solutions is being studied. Initial yields of decomposition products are being determined for solutions containing 40 to 300 g U/l that have been irradiated in a reactor at temperatures from 30 to 150°C.

REDUCTION OF SULFATE BY GAMMA RADIATION

A preliminary study has been made of the formation of SO_2 from gamma-irradiated sulfuric acid and uranyl sulfate solutions. The technique involved sweeping a solution with helium gas during irradiation and measuring the SO_2 formed by change in extinction of the dilute ceric sulfate solution through which the gas was bubbled. SO_2 was produced in 95% H_2SO_4 (approx. 18 M) and 11.0 M H_2SO_4 , but none was detected from 0.4 M H_2SO_4 or 1.25 M UO_2SO_4 solutions.

INITIAL YIELDS OF GAS FROM REACTOR-IRRADIATED URANYL SOLUTIONS

Initial gas yields have been obtained for sulfate solutions containing natural uranium at concentrations of 44.6 and 297 g U/l irradiated in hole 12 of the X-10 graphite reactor at 30, 100, and 150°C. Initial gas yields have also been obtained for uranyl fluoride solutions containing 44.6 and 297 g U/l irradiated in the reactor at 30°C. The 297 g U/l uranyl sulfate solution was obtained from W. L. Marshall and had been prepared by the method of Marshall

and Lietzke. The solid uranyl fluoride was a Harshaw product, which was also from W. L. Marshall. Dilutions were made with highly purified water. Irradiations were made in 19-mm-OD silica tubes using 1.8 ml of solution and 3 to 4 cm^3 of gas space.

Figures 12, 13, 14, and 15 show production of H_2 and O_2 as a function of irradiation time. A small amount of gas that was condensable at liquid-nitrogen temperature was always observed. The amount was independent of dose and probably represented CO_2 formed from impurities present in solution.

Initial yields of hydrogen are listed in Table 17.

An excess of hydrogen was produced, and for exposures above 100°C this

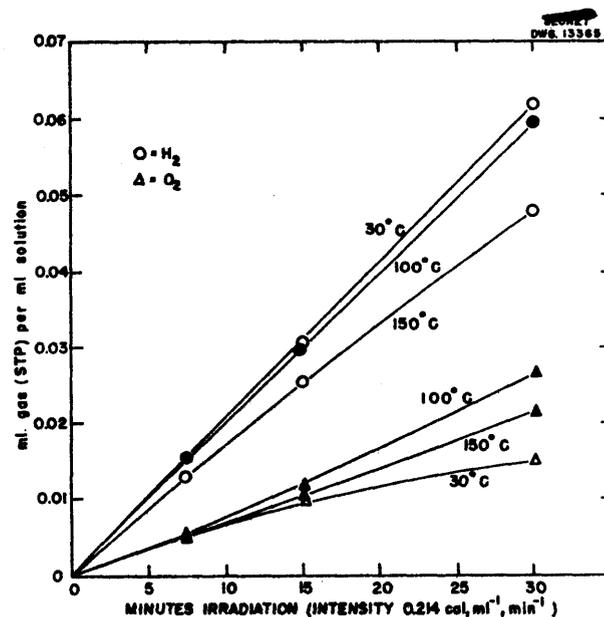


Fig. 12. Gas Production from Reactor-Irradiated UO_2SO_4 Solutions Containing 44.6 g U/l.

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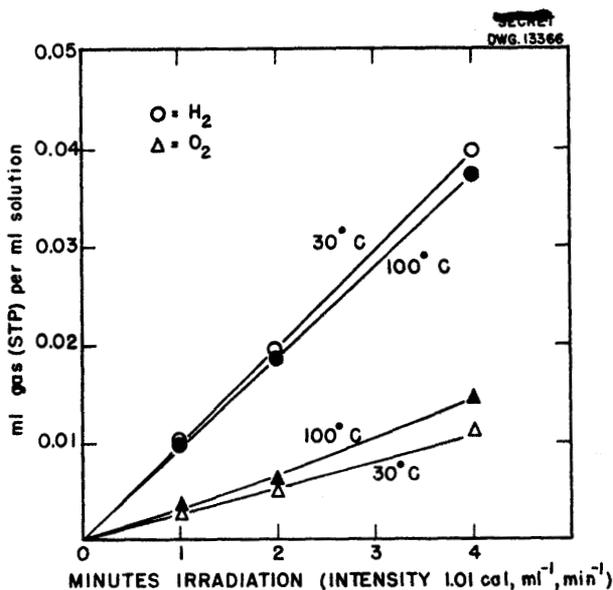


Fig. 13. Gas Production from Reactor Irradiated UO_2SO_4 Solutions Containing 297.0 g U/l.

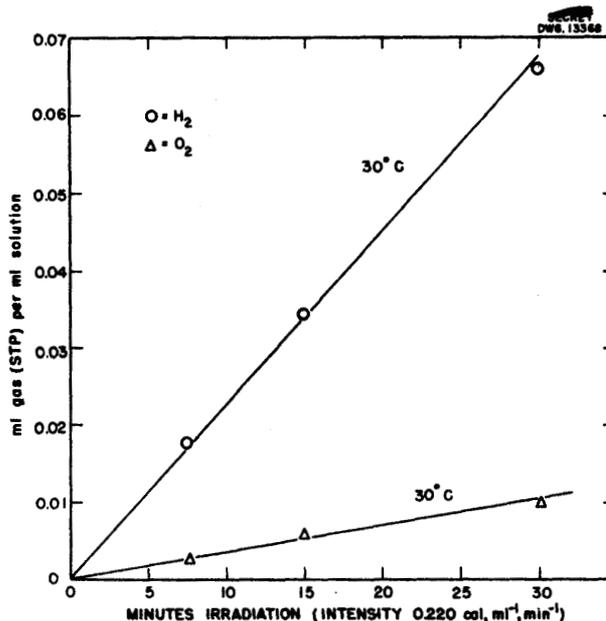


Fig. 15. Gas Production from Reactor Irradiated UO_2F_2 Solutions Containing 44.6 g U/l.

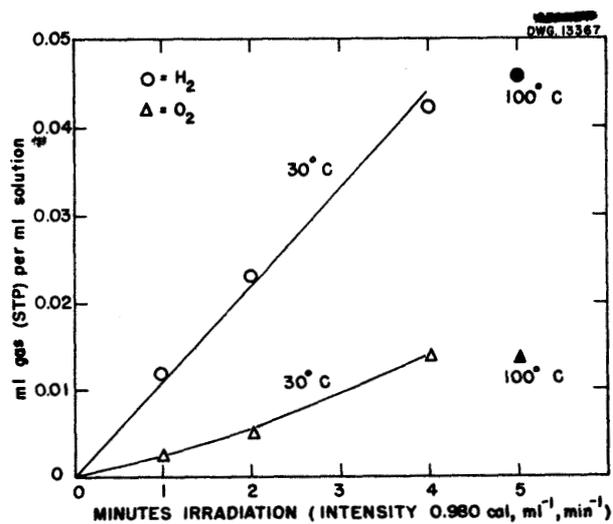


Fig. 14. Gas Production from Reactor Irradiated UO_2F_2 Solutions Containing 297.0 g U/l.

excess became nearly constant after a short irradiation time. The excess probably corresponds to the formation of a peroxide in solution that is unstable at temperatures above 100°C. The excess hydrogen was considerably

greater for irradiations at 30°C than at the higher temperatures. A solution containing 44.6 g U/l and irradiated for 15 min at 30°C was titrated with ceric sulfate. The peroxide formed was approximately equivalent to the excess hydrogen. A light-colored precipitate, presumably uranium peroxide, formed in fluoride solutions containing only 44.6 g U/l and irradiated in the reactor at 30°C. No precipitate formed when similar solutions were irradiated at 100°C. Also, no precipitate formed in fluoride solutions containing 297 g U/l and sulfate solutions containing 44.6 g/l when irradiated at 30°C. The peroxide may be more soluble at the lower pH's of these latter solutions.

MEASUREMENT OF RATE OF ENERGY ABSORPTION IN H_2O AND IN URANIUM SOLUTIONS IRRADIATED IN THE REACTOR

In order to calculate a yield for products obtained on irradiating

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Table 17

**Initial Yields of H₂ from Solutions of Natural Uranium Irradiated
in the Reactor at Several Temperatures**

SOLUTION	COMPOSITION		G _{initial H₂} (molecules/100 ev)		
	g U/l	g U ²³⁵ /l	30°C	100°C	150°C
UO ₂ SO ₄	44.6	0.316	0.98	0.94	0.76
UO ₂ SO ₄	297.0	2.11	1.01	0.95	
UO ₂ F ₂	297.0	2.11	1.16	0.97	
UO ₂ F ₂	44.6	0.316	1.03		

Table 18

**Energy Absorption in Uranyl Solutions Irradiated in the
Maximum Flux in Hole 12 of the X-10 Reactor**

U (g/l)	U ²³⁵ (g/l)	TEMP. (°C)	SOLUTION DENSITY ^(a) (g/ml)	SOLUTION SPECIFIC HEAT ^(b) (cal/g/deg)	RATE OF TEMP. RISE (°C/min)	PILE POWER (mev)	RATE OF ENERGY ABS. IN SOLUTION (cal, ml ⁻¹ , mw min ⁻¹)
0.0	0.0	38	1.00	1.00	0.076	3.85	0.0202
44.6 ^(c)	0.316	37	1.06	0.95	0.201	3.65	0.0582
297.0 ^(c)	2.11	33	1.39	0.73	0.888	3.55	0.265
42.32 ^(d)	39.44	38	1.06	0.95	12.8	3.80	3.55

(a) Data from Lietzke, Wright, and Marshall (August, 1951)

(b) Data from *Project Handbook*, Vol. I, CL-697. Sulfate solution assumed to have approximately the same specific heat as nitrate solution.

(c) Sulfate solution

(d) Nitrate solution

uranyl solutions in the reactor, it is necessary to know the total energy absorbed in solution from gamma rays, neutrons, and fission fragments. The rates of energy absorption in water and in solutions containing three concentrations of uranium-235 were measured using an adiabatic calorimetric method. The calorimeter and method were similar to those used

previously for gamma rays.⁽¹⁾ The results are listed in Table 18. The fission energy absorbed in solution was also calculated from the thermal flux determined using a manganese monitor. The value obtained by this

⁽¹⁾B. S. Borie, Jr., *The Crystal Structure of UAl₄*, ORNL-810, p. 121.

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method was 6% lower than the calorimeter value.

Relative doses received by samples were checked by monitoring the gamma activity of the samples after several day's cooling time.

The calorimetric value measured for the enriched solution is approximately 25% below that obtained by extrapolation of the values measured for the natural uranium solutions. This can be accounted for in part by self-shielding in the solution and in a precipitate that was observed when the calorimeter was opened. The value obtained for water is close to that reported by Ghormley,⁽²⁾ 0.020 cal, ml⁻¹, mw min⁻¹, and that of Richardson,⁽³⁾ 0.0209 cal, mw min⁻¹.

DISCUSSION

The yields reported here are low compared with the reported⁽⁴⁾ yields of 2 to 3 molecules H₂ per 100 ev for alpha-particle decomposition of water. In the solutions containing 40 g of natural uranium per liter only about 60% of the energy absorbed comes from fission recoils. Most of the remaining energy absorption comes from fast neutrons and gammas, which probably induce significant back reaction. The decrease in yield with increase in temperature may also result from enhanced back reaction. The actual amount of back reaction occurring will be studied by measurements of gas yields from solutions in

which back reaction has been suppressed by addition of bromide ion.

The effect of radiation intensity will be studied using various enrichments of uranium-235.

EFFECT OF RADIATION ON HETEROGENEOUS CATALYSTS

J. A. Wethington E. H. Taylor

Further confirmation has been obtained of the loss in activity suffered by ZnO catalysts irradiated with cobalt-60 gamma rays. A sample was irradiated several times in succession, and the activity was measured after each irradiation, with the results shown in Table 19.

The activity is clearly decreasing with successive irradiations and appears to be leveling off at a value different from zero. If this is confirmed it would be an argument against poisoning by water or polymerized ethylene as an explanation for the effect, since either of these would be expected to reduce the activity to zero at a fairly constant rate.

A conclusive proof that the effect is in the catalyst itself rather than a poisoning by polymerized ethylene, would, of course, be the irradiation of a freshly activated catalyst (not exposed to ethylene before irradiation), and subsequent demonstration of a lower catalytic activity than that of a comparable, nonirradiated sample. So far this has been precluded by the irreproducibility in initial activity in successive samples supposedly identically activated. A similar approach, with which preliminary results have been obtained, uses the observation previously reported that irradiation restores the heat sensitivity to a sample previously annealed to a constant activity. The procedure here was to

(2) J. R. Coe and E. H. Taylor, *Report of the Chemistry Division for the Months March, April, and May 1947*, MonN-311.

(3) D. M. Richardson, *Calorimetric Measurement of Radiation Energy Dissipated by Various Materials Placed in the Oak Ridge Pile*, ORNL-129.

(4) F. C. Lanning and S. C. Lind, "Chemical Action of Alpha Particles from Radon on Aqueous Solutions," *J. Phys. Chem.*, 42, 1229-47 (1938).

FOR PERIOD ENDING SEPTEMBER 30, 1951

Table 19

Effect of Irradiation upon Activity of ZnO Catalysts
toward Hydrogenation of Ethylene

TOTAL TIME OF IRRADIATION (hr) (At about 15,000 r/min)	FIRST-ORDER RATE CONSTANT FOR $2\text{H}_2 + \text{C}_2\text{H}_4$ AT 0°C , hr^{-1}
0	1.55×10^{-2}
144	1.30×10^{-2}
238	1.07×10^{-2}
1218	0.78×10^{-2}

activate two samples simultaneously and then anneal them identically at 100°C under vacuum, check the activity of one of the samples occasionally to monitor the progress of the annealing, and continue to anneal both well

beyond the time when the activity of the one became constant. The other sample was then irradiated and tested for activity during further annealing at 100°C . The results are given in Table 20.

Table 20

Effect of Irradiation of a ZnO Catalyst upon Its
Susceptibility to Annealing at 100°C

TREATMENT	CATALYTIC ACTIVITY, FIRST-ORDER RATE CONSTANT FOR $2\text{H}_2 + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_6$ AT 0°C , hr^{-1}	
	Sample 1	Sample 2
Activation	1.61×10^{-2}	Annealed like Sample 1, but not contacted with $2\text{H}_2 + \text{C}_2\text{H}_4$
Anneal overnight at 100°C	1.45×10^{-2}	
Anneal 915 min more at $100-110^\circ\text{C}$	1.33×10^{-2}	
Anneal 995 min more at $100-110^\circ\text{C}$	0.89×10^{-2}	
Anneal 698 min more at $100-110^\circ\text{C}$	0.89×10^{-2}	
Irradiate Sample 2 for 275 hr at about 15,000 r/min with Co^{60} gammas		1.20×10^{-2}
Anneal 15 min at 100°C		1.15×10^{-2}
Anneal 30 min (total) at 100°C		1.05×10^{-2}
Anneal 90 min (total) at 100°C		1.02×10^{-2}
Anneal 180 min (total) at 100°C		1.02×10^{-2}
Anneal 1025 min (total) at 100°C		0.90×10^{-2}
After standing 23 days at about 0°C	0.87×10^{-2}	

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If the results can be accepted at their face value, it is clear that Sample 2, presumably brought to a constant activity by annealing at 100°C prior to irradiation, was made susceptible by irradiation to further annealing at the same temperature.

It is hoped to improve the reproducibility of initial activities by activation at higher temperatures. If this is achieved, satisfactory evidence as to the origin of the effect should be forthcoming by either of the methods described here.

CHEMISTRY OF THE SOLID STATE

HIGH-TEMPERATURE X-RAY DIFFRACTION
SPECTROMETER

M. A. Bredig

With the improved graphite heating element a temperature of 2100°C was reached with a power input of approximately 6 kw. The heat shield also has been redesigned. Further development work is needed on the sample support.

REMOTE-CONTROL X-RAY DIFFRACTION
SPECTROMETER

M. A. Bredig G. E. Klein**
B. S. Borie, Jr.* F. A. Sherrill**

The main parts of the instrument have been received from the research shops and the apparatus is temporarily set up in front of one of the "hot" cells of the Physics of Solids building. The X-ray tube, the proportional counter tube and circuits, and the monochromator crystal are being installed. Extensive testing of all these parts and of the complete instrument is the next task. This will be completed before actual operation in the "hot" cell.

EFFECTS OF RADIATION ON
CRYSTAL STRUCTURE

M. A. Bredig D. S. Jesseman

LEAD OXIDE

Word has been received from Chalk River that unfortunately the second series of samples that were to be irradiated for a dosage of four times that of the first series has been lost there. Preparations are being made to repeat the test, and to check

in as many ways as possible the tentative conclusions reached on the basis of the first test.⁽¹⁾ Two samples of yellow oxide, one of commercial origin, the other prepared by precipitation on rapid cooling from a hot solution in 10 N potassium hydroxide, and one sample of the red modification, prepared by boiling commercial oxide in a similar solution, are being irradiated in the fast-neutron facility of the LITR.* The fast flux is assumed to be at present approximately 20 times that of hole 51 of the X-10 graphite reactor where no effect had been observed in 3-weeks irradiation, and is about one-half of the fast flux of the Chalk River facility where an effect was obtained.

Also included in this test are one sample each of the calcite and the aragonite modifications of calcium carbonate in powder form. All samples are enclosed in sealed pyrex-glass ampules. Cooling, i.e., heat transfer to the water-cooled aluminum-metal torpedo holding the ampules, is provided by filling the remaining space in the torpedo hole with distilled water. Crystal phase transformation by plastic deformation is known not to occur in calcium carbonate crystals. Therefore, if such transformation did occur on fast-neutron bombardment, it would either be in direct contradiction to the conclusions of the first lead oxide experiment, or it would indicate an undesired rise in ambient temperature

*The cooperation of T. H. Blewitt and R. R. Coltman, Jr., of the Physics of Solids Institute, who designed and operate this facility is gratefully acknowledged.

⁽¹⁾M. A. Bredig, "Effects of Radiation on Crystal Structure," *Chemistry Division Quarterly Progress Report for the Period Ending June 30, 1951*, ORNL-1116.

*Metallurgy Division

**Physics of Solids Institute

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above 400°C, the transition temperature for the reaction aragonite \rightarrow calcite, which would also invalidate those conclusions.

In order to check results obtained by earlier investigators⁽²⁾ several samples of the yellow and red forms of lead oxide were irradiated for several hours (2 to 20) with the ultraviolet light of a quartz mercury lamp, with X rays (35 kv, 20 ma, copper anode) and with gamma rays. With X-rays, commercial yellow oxide which had shown the transformation into the red form in the first Chalk River exposure changed color towards an orange brown, in apparent accordance with the microscopic observations of Hofman. However, an X-ray diffraction pattern did not show any trace of the red form, whereas a pattern of a specimen colored to a similar shade by grinding in a mortar shows considerable quantities of this latter modification to be present (Figs. 16 and 17). This result confirms the statement made in the previous report that no real evidence was available, prior to the recent neutron bombardment for this type of phase transformation to occur on irradiation. The color change to brown on irradiation with X-rays must be due to F-center formation. In addition, the diffraction lines of metallic lead, of minium, and of an additional phase, as yet unidentified, appeared in the pattern of the specimen of the commercial yellow oxide after irradiation with ultraviolet light while the color changed to a dark grey. It is interesting to note that no such changes were observed with the red form or with the variety of the yellow one made in the laboratory as described above. An explanation of these differences in behavior, par-

(2) J. Hoffman, "Anderungen der Bleioxyde durch Licht and Druck," *Z. anorg. Chem.*, 228, 160-8 (1936).

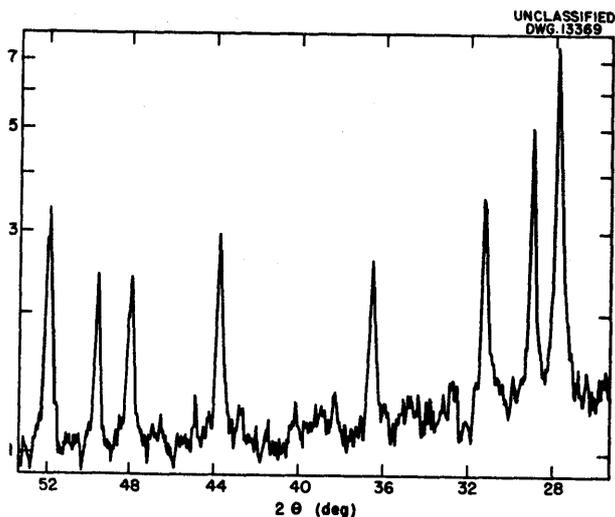


Fig. 16. X-ray Diffraction Pattern of Yellow Lead Oxide Before and After Exposure to X-ray (5×10^7 r).

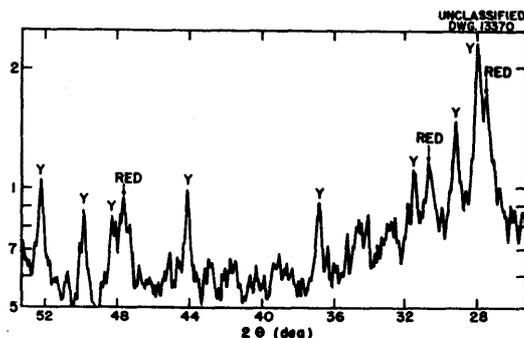


Fig. 17. X-ray Diffraction Pattern of Yellow Lead Oxide Ground in a Mortar.

ticularly in the case of X-rays, is not readily at hand.

Exposure of one red and one yellow lead oxide sample, the latter the laboratory-made variety, for three months or a total dosage of approximately 10^9 in the large cobalt gamma source in the canal at X-10 did not produce any change visible to the eye or in the X-ray pattern of the

yellow specimen, whereas a change to brown without change in X-ray pattern occurred in the red specimen. If it is remembered that the gamma flux in the Chalk River test was probably one hundred times larger, it seems clear that the negative result in the cobalt source does not permit the conclusion that gamma rays did not participate in the transformation of the yellow form in the Chalk River experiment. Another test with higher gamma-ray dosage is needed to decide this question.

ORGANIC ACID SALTS

Examination of samples of sodium bitartrate tetrahydrate, sodium binoxalate monohydrate, and arsenous oxide that had been exposed to approximately 10^9 in the cobalt gamma-ray source did not reveal any change to the eye or in the X-ray pattern. However a considerable gas pressure, presumably of hydrogen and/or carbon dioxide, was found to have built up in the ampule, indicating some decomposition. This decomposition was insufficient to bring about destruction of the crystal structure.

FUSED SALT - EXCESS METAL SYSTEMS

M. A. Bredig J. W. Johnson

The experimental investigation of the solubility of alkali metals in their fused and/or solid halides has been started. Stainless steel tubes containing sodium metal and sodium fluoride-potassium fluoride eutectic (60 mol % KF), lithium metal and lithium fluoride, and sodium metal and sodium chloride were heated to various temperatures for varying periods of time and then quenched. The tubes were cut open with a tube cutter and the salt phase separated from the free metal by hand picking. The salt

phase was analyzed for metal content by placing it in distilled water and, after the reaction ceased, titrating the solution with HCl to determine total alkalinity. This method is subject to error if alkali metal oxide, hydroxide, or hydride, instead of free metal is present, since alkalinity will be developed in the water solution in these cases also. A second although minor source of error in the case of lithium fluoride is the possibility of incomplete extraction of the lithium metal due to the relative insolubility of lithium fluoride in water. These errors can and will be minimized in future more precise tests by measuring the quantity of hydrogen evolved in addition to the determination of the alkalinity, by complete analysis for halide and total metal contents, and by the use of longer extraction times for LiF melts.

Some solubility, in the vicinity of 5 at. %, was found in the case of lithium and lithium fluoride at temperatures between 900 and 1000°C. Somewhat inconclusive results were obtained with sodium and NaF-KF eutectic due to the replacement of potassium in KF by sodium, formation of a sodium-potassium alloy, and formation of a NaF-enriched fluoride phase that was not liquid at the temperature of the experiment. Solubility of sodium in sodium chloride was found to be 4 at. % at 850°C, in disagreement with the findings of previous investigators who obtained a figure of 15 at. %.⁽³⁾

Improvements in apparatus and methods are now being made in an effort to obtain more precise results.

⁽³⁾R. Lorenz and R. Winzer, "Die Löslichkeit von Natrium und Calcium in ihren Chloriden und Chloridgemischen," *Z. anorg. Chem.*, 183, 121-6 (1929).

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MISCELLANEOUS X-RAY DIFFRACTION WORK

M. A. Bredig R. D. Ellison

Primarily to relieve the X-ray group of the Metallurgy Division of part of their excessive burden of

identification work, problems originating in the Chemistry and Chemical Technology Divisions were handled. These problems consisted mainly of identification of uranium and plutonium compounds used in connection with the development of a homogeneous reactor.

INSTRUMENTATION

SCINTILLATION COUNTER WITH HIGH
GAMMA-COUNTING EFFICIENCY

C. J. Borkowski

Full exploitation of the high intrinsic efficiency of scintillation counters for the detection of gamma rays requires that a crystal must be used that has a high density, preferably a high atomic number, a large light output per unit gamma-energy loss in the crystal, and good optical properties. At present only sodium iodide activated with thallium iodide meets these requirements. Measurements made on several type-5819 photomultipliers and sodium iodide crystals indicate that about 400 ev gamma-energy loss in the crystal is required to release a single photoelectron from the photocathode. Since the number of dark current pulses is practically zero at a bias setting corresponding to ten photoelectrons, at this bias all Compton electrons and photoelectrons are counted that exceed an energy of 4 kev. The number of pulses corresponding to 4 kev or less is small, so a plateau or at least a region of minimum slope should be observed in an integral bias curve. Figure 18 shows the plot of the counting rate as a function of the photomultiplier voltage for various energy gamma rays using a sodium iodide crystal $1\frac{1}{2}$ in. in diameter and 2 in. long. At a voltage corresponding to a bias of 20 kev the counting rate is rather insensitive to photomultiplier voltage variations of the order of a few per cent. Thus reproducible counting can be done over long periods of time.

DESCRIPTION OF SCINTILLATION COUNTER

It is believed that whenever possible all measurements of radioac-

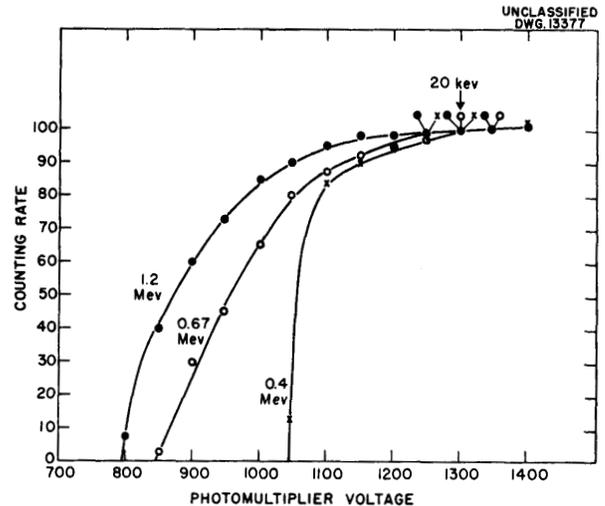


Fig. 18. Counting-Rate Voltage Plateau for the High-Efficiency Gamma Scintillation Counter.

tivity should be made by gamma counting of liquid or solid samples. The counter designed for this purpose (Fig. 19) is similar in principle to the calcium fluoride counter described in ORNL-607.⁽¹⁾ The sodium iodide crystal is $1\frac{1}{2}$ in. in diameter and 2 in. long and has a concentric $\frac{5}{8}$ -in. hole $1\frac{1}{2}$ in. deep drilled in it. The end of the crystal is machined to fit the curvature of the photocathode of the type-5819 photomultiplier. Silicone high-vacuum grease is used to optically couple the crystal to the photomultiplier. Powdered magnesium oxide is used as a reflector for all sides of the crystal. An aluminum housing fits over the crystal and the photomultiplier, and is hermetically sealed to the glass envelope with Apiezon Q. A brass or stainless steel can is slipped over the aluminum housing to

⁽¹⁾R. S. Stone and C. J. Borkowski, "Calcium Fluoride as a Scintillation Counter," *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1949*, ORNL-607, p. 168.

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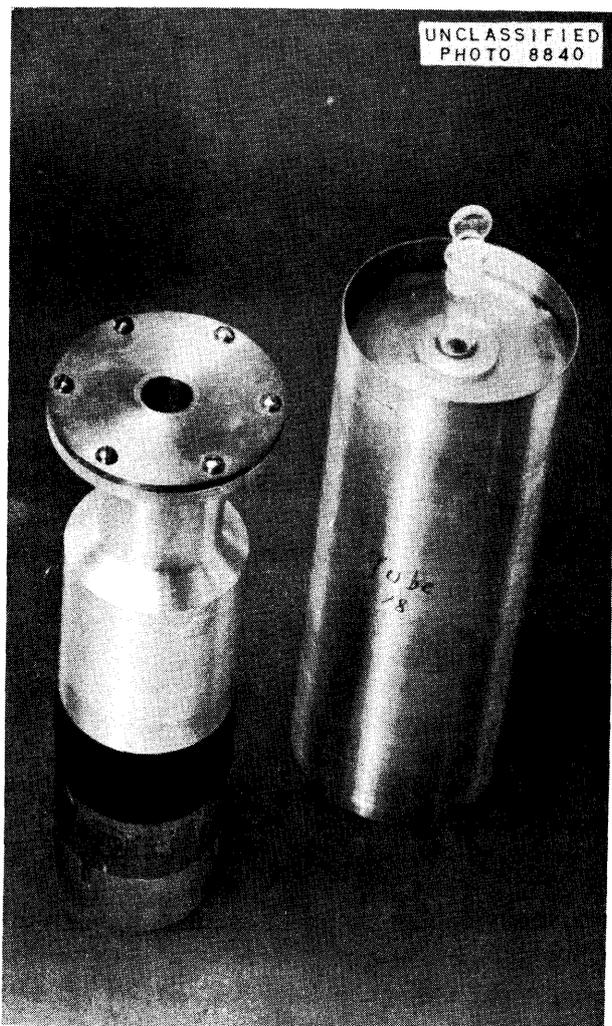


Fig. 19. Scintillation Counter.

prevent contamination of the assembly if a sample is spilled. To prevent the contamination of the hole by test tubes that have external contamination, an aluminum foil liner or plastic insert is used. Two-ml glass test tubes are used for sample containers. The photomultiplier is connected to a nonoverloading amplifier with 10-mv input sensitivity and 0.3- μ sec rise time. A positive high-voltage supply is obtained from a standard G-M scale of 64.

Figure 20 shows the gamma efficiency of this counter as a function of

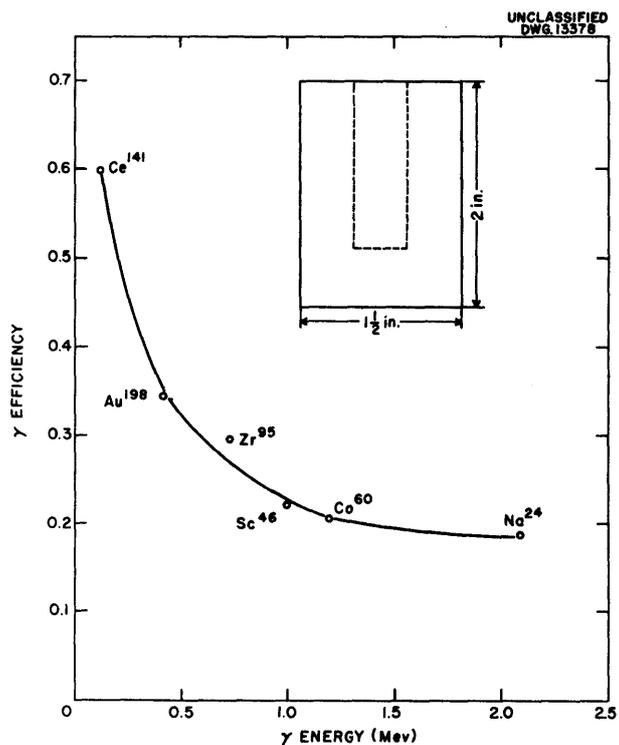


Fig. 20. Gamma Efficiency of NaI-LiI Scintillation Counter.

energy. It can be seen that the gamma-counting yield is as high or higher than conventional beta-counting yields using end-window G-M counters. If two gammas per disintegration are emitted, e. g., as in cobalt-60, the counting yield is not doubled because both gammas are simultaneously absorbed in the crystal and only one pulse is obtained. Thus, if the efficiency for one gamma is 20%, the combined efficiency is $0.2 + 0.2 - (0.2 \times 0.2)$, or 36%.

The high gamma-counting yield, the reproducible geometry, and particularly the ease of sample preparation make this counter exceedingly useful. Three such counters have been in use for a period of four months with no change in their characteristics, indicating that the reflective properties of the sodium

iodide crystal surface were not changing and hence a hermetic seal was obtained.

Some energy discrimination is possible with this counter as can be seen from Fig. 18. By adjusting the photomultiplier voltage to 1030 v, no gammas below 0.4 mev will be counted, and yet 80% of a 0.67-mev gamma will be counted. The energy resolution of the crystal is impaired by the concentric hole. For example, the crystal before the hole was drilled in it gave a 9.0% full width at one-half maximum for a 0.67-mev gamma ray. After drilling the hole the width increased to 15%.

With 2 in. of lead shielding the background at 20 kv bias is 200 c/min.

METHOD FOR DETERMINING THE DEAD TIME OF AN AMPLIFIER OR SCALER

E. Fairstein

The dead time of a counting system is usually determined (1) by the paired-sample technique or (2) with a double-pulse generator.

In the first method the samples are counted separately and then together. Because of losses in the system, the recorded counting rate of the samples together will be lower than the sum of the individual counts. The resolving time can be calculated from this difference.

In practice the method is a lengthy one. The reason will be apparent from the following numerical example.

The resolving time of a proportional counter is to be determined. It is known that the resolving time is in the neighborhood of 6 μ sec. Two samples are available for the test, each of which exhibits a counting rate of 1000 c/sec.

Under these conditions, it can be shown that the difference count will be approximately 12 c/sec. If this number is to be determined to an accuracy such that the standard deviation is not to exceed 10%, or 1.2 c/sec, it will be necessary to determine each of the separate counts to an accuracy such that the standard deviation for each of them does not exceed 0.4 c/sec. This figure indicates that 6×10^6 counts must be accumulated for each reading or a total expended time of over 4 hr.

The results from this test will then indicate the over-all resolving time. It gives no information about the resolving time of the separate components of the counting system.

In the second of the two methods, a signal is supplied to the equipment under test from a pulse generator whose output consists of a double pulse. The time interval between the two pulses can be varied by a calibrated control. As the spacing is increased from zero, a point will be reached where the recorded counting rate doubles. The spacing between the pulses at this point represents the resolving time.

This test tells nothing about the resolving time of the counting tube or chamber, but will give information about each of the electronic components of the counting system. Even this information is of limited value, however, because often signals occurring at a random rate cause difficulties that are not detected by tests with signals occurring at a uniform rate.

DESCRIPTION OF THE NEW METHOD

The method is best described by referring to Fig. 21. The output of a pulse generator and a random-signal source are both applied to

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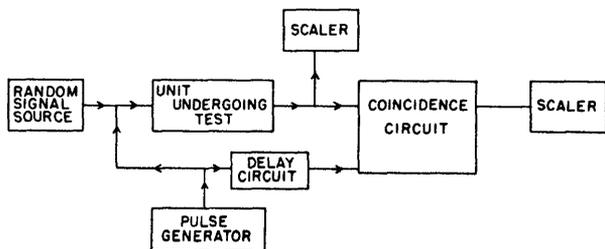


Fig. 21. Block Diagram of Resolving-Time Determination Technique.

the unit under test. The random-signal source may be the chamber or other detector normally used with the instrument. The output from the instrument is applied to one channel of a coincidence circuit. The other channel is supplied from the pulse generator referred to above with a time delay which matches the time delay of the unit under test.

It is necessary that the coincidence circuit have a resolving time shorter than the unit to be tested.

It is evident that if no signals are coming from the random source, every pulse from the pulse generator will be recorded by the output scaler. If the counting rate from the random source is then made high, it will be observed that the recorded counting rate decreases. The decrease is caused by some of the pulses from the random source preceding pulses from the generator by a time interval equal to or less than the resolving time. These pulses cause the test unit to be paralyzed during the interval that a pulse from the generator can activate the coincidence circuit. It can be shown that if the coincidence circuit has a sufficiently short resolving time, the fractional loss in counting rate obtained by this method is numerically equal to the fractional counting-rate loss the unit would exhibit if acted upon by the random source only.

The main advantages of this method over the previously described methods are that every part of the system, except the detector, can be tested under actual counting conditions, and the time necessary for the test is considerably less than for the paired-sample technique. Its greatest disadvantage is that the detector itself cannot be tested.

The saving in time for a measurement can be demonstrated by the following example.

The same unit is to be tested as in the previous case. One of the 1000-c/sec samples will be used as the random source, and a 60-c/sec pulse generator will be used.

From the approximately known dead time, it is known that approximately 0.012 parts of the generator pulses or 0.72 c/sec will be lost. These pulses will be lost at a random rate. If the standard deviation is not to exceed 10%, as in the previous case, it will be necessary to "accumulate" 100 lost counts. This will take less than 3 min. The counting rate of the random source can be determined to an accuracy of 1% in 10 sec. All the necessary measurements can be completed in less than 5 min.

DESCRIPTION OF AN ALTERNATE METHOD

The block diagram of an alternate method appears in Fig. 22. This is a much simpler method because no special equipment is required other than a pulse generator, an oscillograph with a calibrated sweep, and a camera. If the oscillograph has a sufficiently long persistence screen, the camera is not necessary.

In this method the oscillograph sweep is triggered by the pulse generator. The output pulse from the amplifier is sharply defined on the

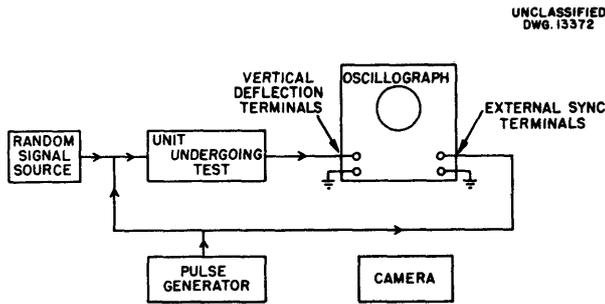


Fig. 22. Block Diagram of Photographic Method for Determining Resolving Time.

screen at the start of the sweep. Random pulses will appear later on the sweep axis. If a photograph is taken of the screen with a long time exposure, the photograph will exhibit the pulse-generator pulse in sharp definition, followed by a clear space, and then a blur of light representing the random pulses. The distance from the beginning of the sharply defined pulse to the beginning of the blurred region represents the resolving time. The accuracy of this simpler method is not as great as can be obtained with the first method.

In principle the pulse generator is not necessary in this second method. The sweep can be initiated by the random-signal source. However, if this is done, it will be found that because of the high counting rate the initial part of the sweep will be so bright that halation will mask the effect to be observed. Also, it will be necessary to have a jitter-free sweep, something not common to all oscillographs.

RESULTS

Both the new and the alternate methods have been tested with excellent results. The new method has already resolved some scaler difficulties which would have been extremely difficult to locate by any other method.

The new method can also effectively determine the energy resolution of an amplifier-discriminator combination as a function of applied counting rate.

A permanent unit containing the necessary coincidence circuit, pulse generator, and scalers is now under construction and should be completed soon.

SCINTILLATION-COUNTER POWER SUPPLIES

E. Fairstein F. Porter

Two power supplies for scintillation counter use have been completed and tested. The high-voltage output of one is positive with respect to ground; the output of the other is negative. A unit that can supply either polarity is not feasible because of hum difficulties and circuit complications.

The circuit diagrams of the supplies are shown in Figs. 23 and 24. The first is a series tube regulator and the second is a shunt regulator. The equivalent circuit of each is that of a cathode follower whose grid-to-ground voltage is the drop across the 1/25-w neon tubes.

The operating characteristics are as follows:

Output voltage - 500 to 1500, adjustable in steps of approximately 57 v.

Maximum load - 1.5 ma at any output voltage.

Rms noise and ripple - 0.01% at 1 ma load. The ripple varies by a factor of 2 from no load to full load.

Regulation to changes in load - The regulation is that associated with an internal impedance of 1000 ohms.

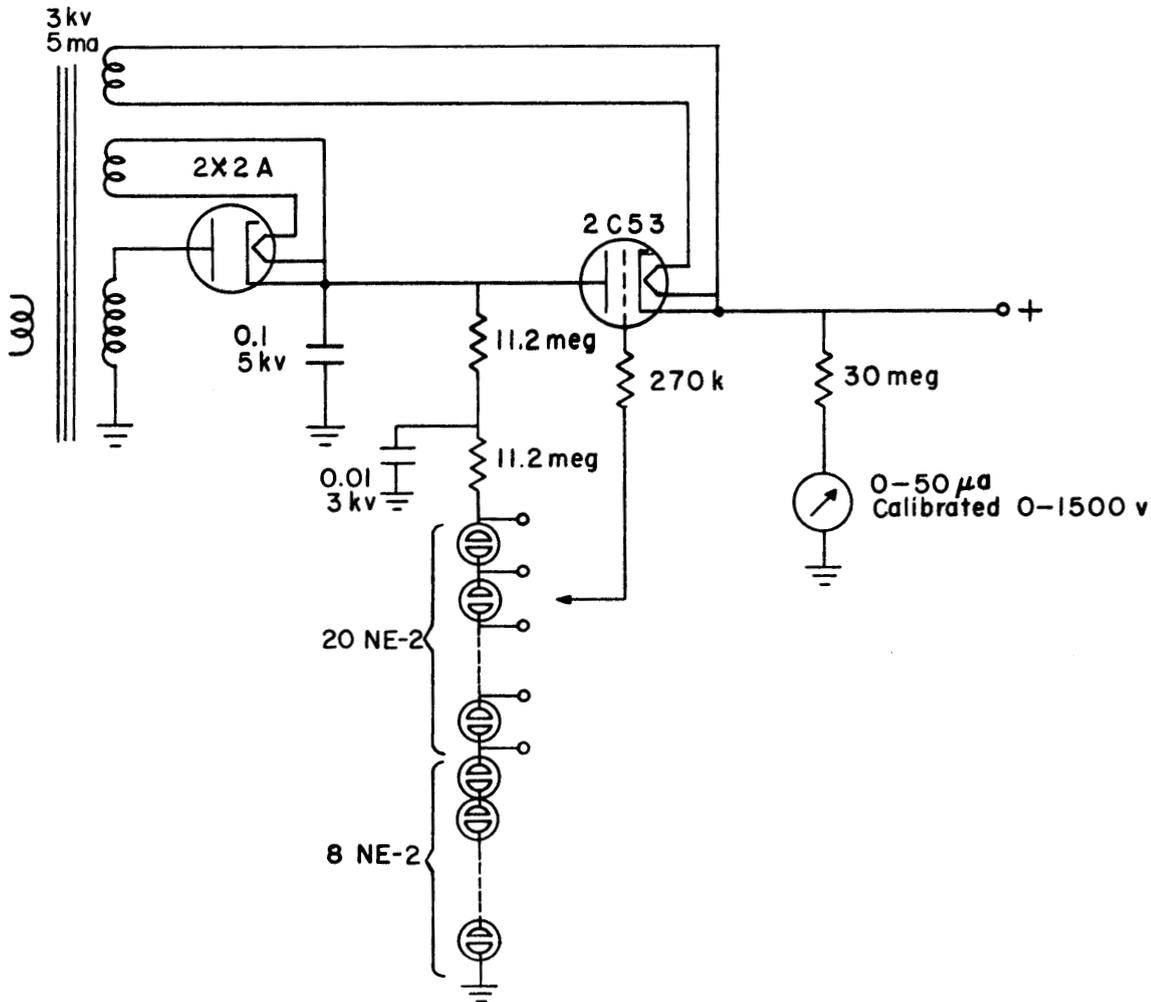


Fig. 23. Positive-Output High-Voltage Power Supply.

Regulation to changes in line voltage -
Line voltage variations are reduced
by a factor of 40.

Stability - The peak-to-peak variation
in output for 12 hr of operation is
approximately 0.01%. The warm-up
drift is about 1%. Long-time sta-
bility figures are not yet avail-
able.

Physical dimensions - The units are
built on chasses whose dimensions
are 5 x 10 x 3 in.

Because of the relatively poor
regulation against changes in line
voltage, it is desirable to operate
the units from a regulated supply
line. The poor regulation is caused
almost entirely by the neon-lamp
characteristics.

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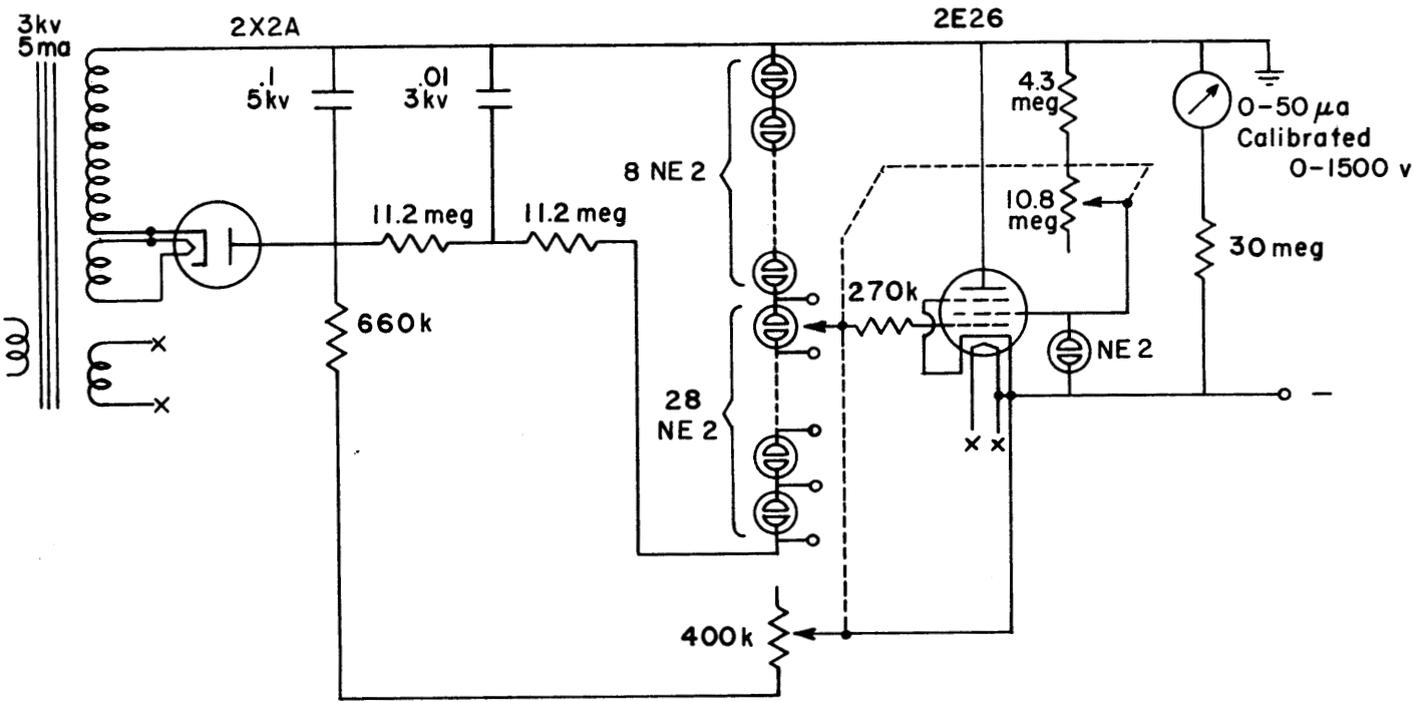


Fig. 24. Negative-Output High-Voltage Power Supply.

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REACTOR CHEMISTRY

ALTERNATE FUEL MEDIA

J. S. Gill H. W. Wright
 W. L. Marshall

The solubility of uranium trioxide in orthophosphoric acid at 250°C has been determined and is reported elsewhere.⁽¹⁾ The data given in Table 21 indicate that an aqueous fuel system at 250°C is of marginal feasibility from a phase-stability and neutron-economy standpoint.

The solid-phase analyses reported in Table 21 are additional data that could indicate a theoretical composition of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 2\text{H}_3\text{PO}_4$. X-ray diffraction patterns were identical for the different solid-phase samples.

A short investigation of the effect of carbon dioxide pressure on the phase stability of sodium uranyl carbonate solutions is reported in the Homogeneous Reactor Project quarterly project report.⁽²⁾ Briefly, hydrolytic precipitation occurs at about 190°C in 0.24 M $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ solutions. The temperature of precipitation was changed only slightly by several atmospheres carbon dioxide pressure.

PLUTONIUM PHASE STABILITY IN AQUEOUS URANYL SULFATE AT 100 TO 250°C

H. W. Wright K. S. Warren
 W. L. Marshall

A full-time investigation is under way on plutonium phase-stability studies in aqueous uranyl sulfate at 100 to 250°C. The problems presently

inherent are (1) the preparation of pure plutonium sulfate and (2) the development of synthetic and analytical techniques for determining characteristics of the solutions above 100°C. The current progress will be given in detail in the Homogeneous Reactor Project quarterly progress report for the period ending November 15, 1951.

FISSION-PRODUCT SOLUBILITIES IN URANYL SULFATE SOLUTION

E. V. Jones

The solubility studies of Lietzke and Stoughton⁽³⁾ on lanthanum and yttrium sulfates in 0.126 M uranyl sulfate have been extended to include data for these two sulfates in 1.26 M uranyl sulfate solution.

Some of the experimental data on yttrium sulfate are given elsewhere.⁽⁴⁾ The completed studies will be reported in a future Homogeneous Reactor Project quarterly progress report.

Investigations are also in progress on the solubilities of cesium sulfate and cerium sulfate in 1.26 M uranyl sulfate.

Preliminary work has been started on the solubility of zirconium sulfate in uranyl sulfate.

CONDUCTIVITY OF URANYL SULFATE SOLUTION

R. D. Brown

The preliminary tasks of obtaining and setting up the necessary apparatus

⁽¹⁾J. A. Swartout, et al., *Homogeneous Reactor Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121.

⁽²⁾*Ibid.*

⁽³⁾M. H. Lietzke and R. W. Stoughton, *The Measurement of the Solubility of Fission Product Sulfates at High Temperatures and Pressures*, ORNL-970.

⁽⁴⁾J. A. Swartout et al., *op. cit.*

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Table 21

Solubility of Uranium Trioxide in Orthophosphoric Acid Solutions at 250°C

SOLUTION			SOLID	
MOLARITY H ₃ PO ₄	MOLARITY UO ₃	MOLE SOLUBILITY RATIO PO ₄ /U	PER CENT PO ₄	PER CENT U
2.77	0.23	12		
3.57	0.42	8.5		
4.86	0.78	6.2		
5.05	0.84	6.0		
5.95	1.26 (?)	-	31.6	59.1
6.05	1.13	5.35		
6.69	1.30	5.15	29.2	55.7
6.95	1.43	4.86	30.6	56.1

Solid Phase at Other Temperatures

TEMPERATURE (°C)	SOLUTION MOLARITY U	SOLID PHASE	
		PER CENT PO ₄	PER CENT U
Room	0.38	31.1	59.5
200	0.23	26.4	60.4
260	1.7	30.0	61.7

(begun by W. L. Bunger, Summer Research Participant from the Alabama Polytechnic Institute) have been largely accomplished, and measurements of the conductivity of uranyl sulfate solutions in concentrations from 0.05 to 1.25 M have been made at 25°C. The results obtained indicate that uranyl sulfate behaves as a weak electrolyte having a conductivity somewhat greater than that reported for uranyl fluoride.⁽⁵⁾ A comprehensive account of this investigation will be given in the Homogeneous Reactor Project quarterly progress report for the period ending November 15, 1951.

VAPOR-PRESSURE STUDIES OF AQUEOUS URANIUM SALTS AND URANYL SULFATE

H. O. Day J. S. Gill

The apparatus for vapor-pressure studies of aqueous uranium salts above 100°C is discussed fully in a previous report.⁽⁶⁾ Vapor-pressure studies of uranyl sulfate (0.126 and 1.26 M) and uranyl nitrate (1.26 M) solutions have been made from 200 to 350°C. The data on the above solutions indicate vapor pressures below that of water, i.e., 5 to 10 psi for the sulfate and 10 to 20 psi for the nitrate. Details, together with data,

⁽⁵⁾G. R. Dean, *Properties of Uranyl Fluoride*, CC-G-2092, September 11, 1944.

⁽⁶⁾J. A. Swartout *et al.*, *op cit.*

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will appear in the Homogeneous Reactor Project quarterly progress report for the period ending November 15, 1951.

RADIATION STABILITY

H. F. McDuffie, Jr.	F. J. Fitch
J. W. Boyle	A. W. Smith
F. H. Sweeton	K. A. Hub*
D. M. Richardson	W. F. Kieffer
J. F. Manneschildt	J. Ruth*
M. D. Silverman	T. H. Handley

HOMOGENEOUS REACTOR PROJECT STUDIES**

Long periods of irradiation (2280 hr) in hole 60 of the graphite reactor failed to cause any apparent deterioration of the uranyl sulfate solutions contained in stainless steel bombs (variously passivated) held at temperatures of 250 to 290°C during irradiation.

Fundamental studies of specific and net gas-production rates of irradiated uranium-containing solutions of various concentrations and enrichments are being carried out intensively. Uranyl sulfate and uranyl fluoride solutions of enrichments ranging from 0.02 to 93.4% and concentrations up to 600 g U/l are being studied at temperatures up to 250°C. It appears that the G value is a function of the degree of enrichment, falling as the enrichment is lowered. This might be expected, since at low enrichments a smaller fraction of the total energy input will appear as fission energy. Preliminary work on the uranyl nitrate system indicated decomposition via attack on the nitrate ion in concentrated solutions (300 g U/l liberating free nitrogen) but

*ORSORT or summer participants no longer in the group.

**Homogeneous Reactor Project studies are summarized briefly here. This work is reported in detail in the Homogeneous Reactor Project Quarterly Progress Report.

normal decomposition (to $2\text{H}_2 + \text{O}_2$) in dilute solutions (40 g U/l).

Studies on a simulated HRE reflector system (ordinary water in carbon steel bombs using trisodium phosphate, sodium hydroxide, and magnesium hydroxide as corrosion inhibitors), in the presence of reactor radiation (hole 12 of the graphite reactor) at temperatures of 100 to 140°C, gave no indication of abnormal gas production, steady-state pressures, or corrosion. Using heavy water in place of ordinary water resulted in the production of large amounts of magnetic iron oxide. However, subsequent tests with heavy water, made by the corrosion group at Y-12, gave similar effects in the absence of radiation. Further radiation testing of the simulated reflector system will be carried out after the nonradiation corrosion effects have been sufficiently studied.

In nonradiation experiments with stainless steel bombs containing uranyl sulfate solutions heated to 275°C, there was no evidence that pretreatment of the bombs with 400-psi oxygen pressure at 275°C added significantly to the protection afforded by the use of 400-psi oxygen pressure during the test.

When solution instability occurs after a short period of heating (producing a black precipitate of uranium oxides and a water-white solution of low pH by the liberation of sulfuric acid) this instability can be reversed and uranyl sulfate solution regenerated if the solution is heated under oxygen pressure.

It was discovered that hydrogen possesses the ability to reduce solutions of uranyl sulfate at temperatures of 250 to 290°C. For this reduction it is necessary to use quartz vessels and have no heterogeneous catalytic material present

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initially. The kinetics of this reaction are being determined, and the implications with respect to the recombination of hydrogen and oxygen are being investigated as reported below.

A survey of the stability of possible HRE fuel solutions in contact with titanium, zirconium, and pretreated stainless steel has been made at 250°C using quartz ampoules containing the solution and a small piece of metal rod. Visual observation after successive periods of heating has been helpful in establishing the onset of corrosion. Concentrations of 300 g U/l have been used. Titanium appears much more resistant than zirconium or stainless steel to uranyl sulfate and uranyl nitrate solutions both in the presence and absence of air. Chromate pretreated stainless steel and titanium appear more resistant to uranyl fluoride than nitrate-pretreated stainless steel. Zirconium has no resistance to uranyl fluoride.

Apparatus for studying radiation effects at high temperatures and pressures in the LITR, using gamma and neutron fluxes much higher than those obtainable in the graphite reactor, is now ready for final testing and assembly. A vertical facility for short-term tests and two horizontal facilities for long-term corrosion and stability studies are being provided.

HYDROGEN-OXYGEN RECOMBINATION IN SOLUTIONS

The need for better understanding of the reaction between hydrogen and oxygen at high temperatures and pressures has long been evident. All studies of the radiation decomposition of water or aqueous solutions have indicated the importance of the

recombination or "back" reaction as compared with the decomposition or "forward" reaction. Using uranyl sulfate solutions in pretreated stainless steel bombs exposed to graphite reactor radiation at 250°C, an equilibrium is reached after a number of hours at which the forward and back reactions are in balance. The total pressure at equilibrium has been found to be in the range of 2000 to 5000 psi. In arriving at this equilibrium the pressure has frequently gone through a maximum or "over a hump" for unexplained reasons. Tentative explanations for the recombination reaction have included catalysis by the wall of the container, gas-phase homogeneous reaction, liquid-phase radiation-induced reaction, and liquid-phase homogeneous reaction. Until the past quarter no nonradiation experiments had been conducted to test these theories but during the present quarter two lines of work have contributed significantly.

First of all, it was found, as reported above, that hydrogen alone would reduce uranyl sulfate solutions to black oxides and a water-white solution of low pH. It was also found that oxygen could reverse this reduction to regenerate the uranyl sulfate solution. Adding these two demonstrated reactions together gives, as a net effect, the recombination of hydrogen and oxygen with uranyl ion as a catalyst. Second, as a direct test of the theory, stainless steel (untreated) bombs were heated to temperatures of 200 to 290°C in the presence of high pressures of a 2:1 mixture of hydrogen and oxygen. Using empty bombs, or bombs partially filled with distilled water, no substantial amount of recombination was observed. When, however, uranyl sulfate solutions were present there was evidence (in pressure drop) of recombination at substantial rates. At the conclusion of the experiments

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the uranyl sulfate solutions were recovered apparently unchanged. The simple reaction appears to be explained satisfactorily by the following expression:

$$-\frac{dP}{dt} = k_1 (\text{UO}_2^{++}) P \frac{\frac{V_1}{V_g}}{\frac{V_1}{V_g} + \frac{\alpha}{RT}},$$

where

$-dP/dt$ = loss in pressure of hydrogen per unit time (hr) (psi),

(UO_2^{++}) = concentration (or activity) of uranyl ion,

P = pressure of hydrogen (psi),

V_1 = volume of liquid in the system at the temperature of the experiment,

V_g = volume of gas in the system at the temperature of the experiment,

α = constant relating the partial pressure of hydrogen to the molar concentration of hydrogen in the solution at the temperature of the experiment,

R = gas constant, 1.206 cc-psi/deg,

T = absolute temperature.

For convenience the total pressure instead of the partial pressure of hydrogen can be used if a 2:1 mixture of hydrogen and oxygen is used in the experiment. If some other mixture were used, the partial pressure of hydrogen would have to be followed,

as the composition of the gas would change during an experiment.

Using this expression for the kinetics, values of k were obtained for uranyl sulfate solutions at concentrations of 0.125 and 1.25 M over a temperature range of 250 to 290°C. These values are plotted as $\log k$ vs. $1/T$ in Fig. 25 to show the temperature dependence of the reaction. The scatter for the values at high temperature and low concentration indicated that some additional factor was influencing the results. The displacement of the higher concentration line with respect to the lower concentration line may be due to the differences in activity coefficients of the uranyl ion (assumed to be 1.0 in the calculation, but expected to differ).

Previous consideration of the probable mechanism of the reaction had led to the suggestion that other polyvalent metal ions might also catalyze the reaction, and it was suspected that corrosion of the stainless steel bomb might have caused the introduction of such ions and lead to the erratic results. Since nickel (one of the corrosion products of type-347 stainless steel) was known to remain in solution and unhydrolyzed at the temperatures of our experiments, some test runs were carried out using uranyl sulfate solutions containing 460 ppm of nickel. No increase in the rate of recombination was noted in these runs. Further consideration of the potentials involved in going from the oxidized to the reduced state indicated that a catalyzing ion should be reducible by hydrogen gas and oxidizable by either oxygen gas or uranyl ion. Not knowing the values for these potentials at 250°C led to examination of the potentials at 25°C and the choice of copper as the first ion for testing. This choice proved very

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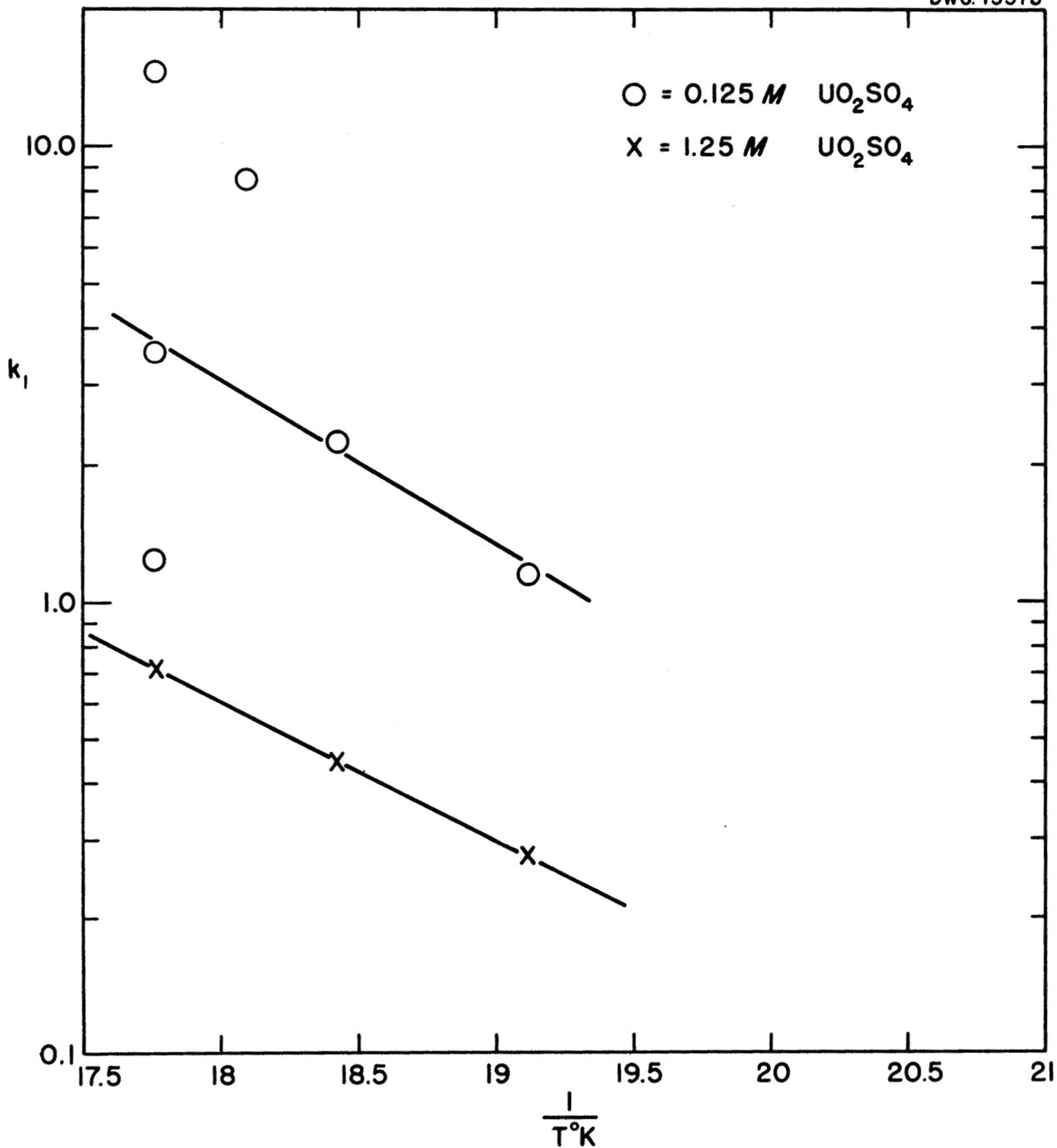


Fig. 25. Temperature Dependence of the Recombination of Hydrogen and Oxygen in the Presence of Uranyl Sulfate Solutions.

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fortunate, as copper appears to catalyze the reaction very strongly. Using 0.125 M uranyl sulfate containing 400 ppm of copper, values of k for copper were calculated over a range of temperatures from 205 to 290°C from the following kinetic expression:

$$-\frac{dP}{dt} = [k_1(\text{UO}_2^{++}) + k_2(\text{Cu}^{++})^2]P \frac{\frac{V_2}{V_g}}{\frac{V_2}{V_g} + \frac{\alpha}{RT}}$$

based on the assumption that the reduction is much slower than the re-oxidation and that the equation for the reaction with copper is



The temperature dependence of the reaction with copper is shown in Fig. 26.

Activation energies for the reaction with uranyl sulfate, at both concentrations, and the reaction with copper appeared to be approximately the same (-15 kcal). The discovery that copper is such a powerful catalyst compared with uranyl ion ($k = 135,000$ at 250°C vs. 1.163 for uranyl ion at the same temperature) has led to a possible explanation for the erratic results obtained with some of the uranyl sulfate solutions; very small amounts of copper may have been introduced inadvertently from some copper-plated nuts used to secure the fitting to the bomb (the plating becomes oxidized to copper oxide, and a small amount could be rubbed off and eventually fall into the interior of the bomb). Analyses are now being made on all solutions used in prior runs to determine the magnitude of the correction that must be applied, and it is certain that the results with

uranyl solutions not containing copper will have to be rechecked carefully.

It is planned to extend the study to include ratios of hydrogen to oxygen other than 2:1, concentrations of uranyl ion higher and lower than those previously used, catalyzing ions other than copper (V, Ti, Sn, Mn, Ce, Tl), use of catalysts in the absence of uranyl ions, tests with uranyl fluoride as well as sulfate, and combinations of catalysts. In addition, plans are under way to test the ability of copper to increase the recombination rate using enriched uranyl sulfate and reactor radiation to produce the hydrogen and oxygen. The effect of copper will be measured by determining the lowering of the equilibrium pressure at a chosen temperature.

The significance of the catalyzed recombination reaction with respect to operation of homogeneous reactors is being considered.

SOLUBILITIES OF FISSION-PRODUCT SULFATES

B. Zemel

The solubility study of the fission-product sulfates in uranyl sulfate solution as a function of temperature is continuing.

The solubility curve for SrSO_4 in UO_2SO_4 has been redetermined, the solubility of silver sulfate in this medium is being determined, and the determination of the solubilities of ruthenium and zirconium sulfates in UO_2SO_4 solution have been undertaken. The last two sulfates present considerable difficulties in attempting to ascertain the species present.

Further details will be given in the Homogeneous Reactor Project quarterly progress report for the period ending November 15, 1951.

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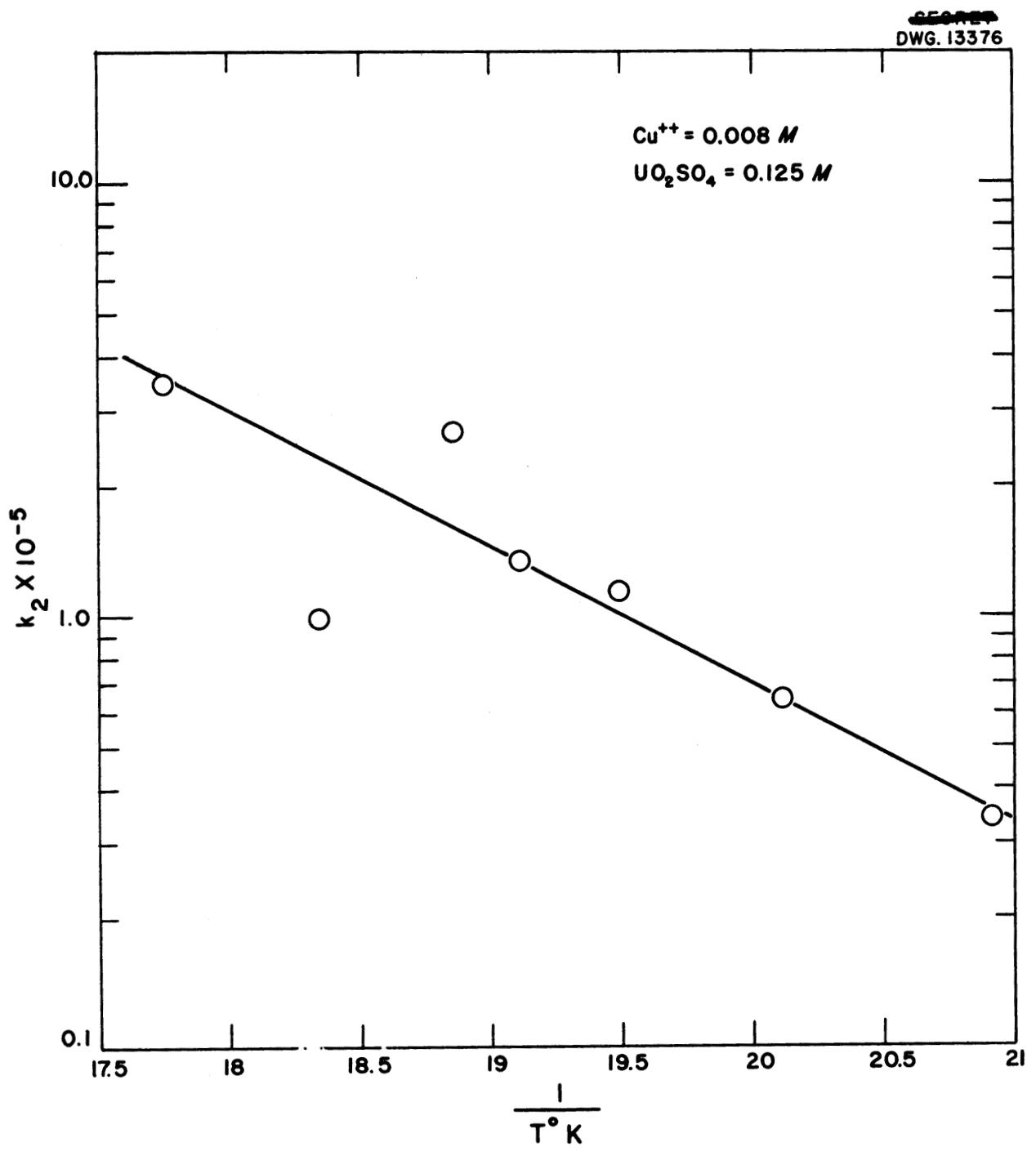


Fig. 26. Temperature Dependence of the Catalysis by Copper Ion of the Recombination of Hydrogen and Oxygen in the Presence of Uranyl Sulfate Solutions.

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HIGH-TEMPERATURE REFERENCE ELECTRODE

M. H. Lietzke R. W. Stoughton

An attempt is being made to develop a reference electrode that can be used at high temperatures (up to 250°C) in connection with corrosion studies for HRE. Such an electrode could be used to follow the potential of stainless steel during the passivation process as well as to check on the quality of a passive film that has been in use.

In preliminary experiments three electrodes will be tried: Pb/PbSO₄, Ag/Ag₂SO₄, and Pt/PbO₂ + PbSO₄. The potentials of these half-cells will be measured against one another as a function of temperature and the values so obtained compared with thermodynamic calculations.

The bomb, heating jacket, and quartz cells have been made. The chemicals and solutions to be used are now being prepared and methods of insulating the wires leading into the cells in the bomb are being investigated. Potential measurements will be started in the near future.

HRE CORROSION PROBLEMS

J. C. Griess

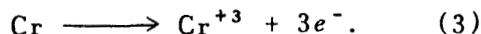
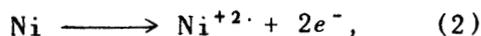
For the past few months the general mechanism of the corrosion process encountered in HRE has been under investigation. The purpose of this study has been to find a means of determining the extent of corrosion when passivated type-347 stainless steel is exposed to uranyl sulfate solutions at 250°C. In all the experiments carried out to date the rate of corrosion has been comparatively slow and the process of determining the relative merits of different protective films has been time consuming. Hence a reliable,

fast method of measuring the effectiveness of different protective films is desirable. If the reactants involved in the corrosion reaction and the corrosion products were known, it might be possible to use changes in the concentration of either as an accurate measure of the corrosion damage. Furthermore, an understanding of the corrosion mechanism might allow a more intelligent attack on the corrosion problem itself.

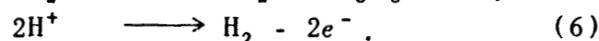
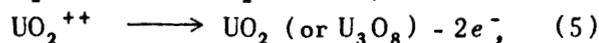
It has previously been pointed out that in the system, uranyl sulfate solution-passivated stainless steel-air, changes in pH, uranyl sulfate, iron, and chromium concentrations do not give a quantitative estimation of the extent of corrosion. It is possible for an analysis of a given solution to show no change after heating at 250°C in a steel vessel even though the steel has been attacked.

The corrosion encountered here is electrolytic in nature and the reactions involved in the corrosion process appear to be as follows:

At the anodic areas



At the cathodic areas



In the presence of oxygen the cathodic reaction consists primarily of the reduction of oxygen. The anodic reactions cannot be identified with certainty since it has not been established that the elements that compose the alloy dissolve in the ratio in which they are present in

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the alloy. If chromium is oxidized it is quantitatively precipitated by hydrolysis. Iron apparently dissolves as ferrous iron, which, in the presence of an oxidizing agent, is also hydrolytically precipitated as ferric oxide. If the nickel in the alloy dissolves, it will remain in solution unless it is carried down with the chromic and ferric oxides. Hence the anodic reactions produce hydrogen ions (by hydrolysis) while cathodic reactions 4 and 6 consume hydrogen ions. Since nickel is the minor constituent of the alloy, and since it should not hydrolyze at the pH values involved, there should be a very slight increase in the pH of the solution as the alloy is corroded. This change in a uranyl solution (pH = 2.5) is so small, however, that it is difficult, if not impossible, to detect unless the corrosion damage has been extensive.

If the corrosion process is slow, the cathodic reaction consists almost entirely of the reduction of oxygen. However, if the corrosion process is comparatively rapid, oxygen may not be able to diffuse to the cathodic surface fast enough to utilize the corrosion currents, and reactions 5 and 6 may take place. Indeed, in three cases where oxygen was present in low concentrations and the protective film on the steel was poor, analysis of the gas phase showed hydrogen to be present, as well as a decrease in the oxygen content. In none of these cases was there a change in the uranium, iron, chromium, or hydrogen ion concentrations of the solutions. The nickel content varied between 10 and 20 ppm.

One experiment has been run in the absence of oxygen. In this particular case hydrogen was found in the gaseous phase and some uranium was precipitated. Ferrous iron and nickel were found in solution and the pH decreased.

X-ray analysis showed that the precipitated uranium consisted essentially of an equimolecular mixture of UO_2 and U_3O_8 . In this case the changes of the various constituents in solution were determined by chemical analysis; then on the assumption that chromium dissolved (i. e., was oxidized) in proportion to its prevalence in the alloy, it was possible to obtain a material balance. The changes in the solution were quantitatively accounted for by using the equations given above.

At this time it appears that the corrosion that occurs at a passivated stainless steel surface on exposure to uranyl sulfate solutions at 250°C is as follows: The protective film itself is chemically inert to the uranyl sulfate solution. However, at weak places in the film, ruptures or crevices develop and the steel itself comes in contact with the uranyl sulfate solution. When this happens, local cells with potential differences as large as 0.3 to 0.5 are possible. In the presence of oxygen the cathodic reaction consists of the reduction of oxygen. At the anodic areas nickelous, ferrous, and chromic ions enter the solution. The chromic ions hydrolyze to yield chromic oxide and the ferrous ions are oxidized and hydrolyzed to ferric oxide. Hence in static systems in the presence of oxygen the precipitation of chromic and ferric oxides tends to stifle the attack before it has proceeded to any visible extent. This process is probably repeated many times over the entire surface. Thus, under the conditions given above, the protective film is self-healing and any corrosion damage is very slight and uniformly distributed over the surface exposed to the uranyl sulfate solution.

In a dynamic system the chance of stifling the attack in the presence

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of oxygen is less, since the ferric ions may be swept away before they are hydrolytically precipitated at the site of corrosion. The above situation should be especially true in regions of great turbulence, and in these regions pitting might result.

In the absence of oxygen, ferrous ions that dissolve are never precipitated due to the basicity of the ferrous ions. Apparently the precipitation of chromic oxide is insufficient to stifle the attack of the uranyl sulfate solution on the steel, and once corrosion begins at given locations attack continues at these areas, the rest of the surface being cathodically protected from corrosion. Since oxygen is not available, the reduction of hydrogen and/or uranyl ions constitutes the cathodic reaction and any reduced uranium hydrolyzes and precipitates. Under the above conditions the corrosion is localized and pits soon become apparent.

While protective films produced on steel by different methods are undoubtedly of different effectiveness, it seems that any film will sooner or later develop breaks or pin holes and that the film must be self-healing to minimize corrosion damage and prevent precipitation of the uranium

from solution. The presence of oxygen in the system certainly is desirable in this respect, but it does not necessarily represent as satisfactory a condition as might be ultimately achieved. For oxygen to be effective, the ferrous ions first formed must be oxidized and then hydrolytically precipitated. While the oxidation is probably fast, the hydrolysis appears to be comparatively slow. Hence, if it were possible to precipitate the ferrous ions as fast as they were formed, the self-healing process would undoubtedly be more effective, and would not depend on the presence of the oxidizing conditions. Similarly an increase in the rate of hydrolysis of ferric ions would facilitate the self-healing process. Future work will be directed along these lines.

The preliminary experiments completed to date indicate that an analysis of the gas phase is the most reliable method of determining the extent of corrosion. Thus the rate of corrosion can be followed by determining the changes in the gaseous phase. By this method it should be possible to determine the relative merits of different protective films and the effectiveness of various inhibitors.

The data as of 1946. The disclosure of its contents by unauthorized person is prohibited.

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